Vol. VII. [APRIL, 1885.] No. 1.

AMERICAN CHEMICAL JOURNAL.

ON THE ACTION OF ALDEHYDES AND AMMONIA ON BENZIL.[1]

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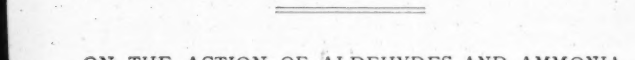
In former communications,[2] relating to the joint action of aldehydes and ammonia on compounds containing the dicarbonyl-group (—CO—CO—), two general reactions of this class have been described:



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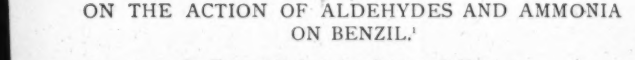
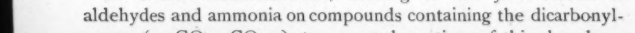


In addition to the above, it was mentioned (Chem. Soc. Journal, 1883, Trans. 17) that with certain aldehydes a third and totally distinct reaction occurs. Thus benzil, salicylaldehyde, and ammonia react according to the equation—



A precisely similar reaction occurs when furfuraldehyde is substituted for salicylaldehyde.

[1] Communicated by the authors.

[2] Chem. Soc. Journ. Trans. 1880, p. 666; 1881, p. 225; 1882, pp. 146, 157 and 323; 1883, pp. 9 and 197.

The present communication is devoted to an account of this new reaction, and to a study of the compound obtained with salicylaldehyde. We venture to think that we have succeeded in throwing light on the constitution of this compound. The general reaction, corresponding with that in which the compound is formed, may be expressed by the following equation:

$$\text{III.}\quad \begin{matrix} X'\text{—CO} \\ | \\ X'\text{—CO} \end{matrix} + 2R'\text{—CHO} + 2NH_3 = \begin{matrix} R'\text{—CH—NH—CO—}X' \\ | \\ R'\text{—CH—NH—CO—}X' \end{matrix} + 2OH_2.$$

This reaction differs from the two foregoing in the fact that whereas in these the two carbon-atoms of the dicarbonyl-group become doubly linked, in the present reaction, as we shall endeavor to show, the atoms undergo separation, so that the diketone is broken up in two halves, which become two substituting acid radicals in the molecule of the new compound; and at the same time the two aldehyde residues become linked by means of the carbon-atoms of the CHO-groups.

In the first two reactions the aldehyde is oxidised at the expense of the diketone; in the third the reverse is the case, and the diketone is oxidised at the expense of the aldehyde. Thus, in the hydrolytic decomposition of the compounds formed in equations I and II, the aldehyde part of the molecule is eliminated as the corresponding acid; in the decomposition of the compounds formed in equation III, the diketone residues are liberated as two molecules of an acid having the same radical as the diketone.

The salicylaldehyde compound was selected for study, partly because of the ease with which it could be prepared, but chiefly on account of the readiness with which the various compounds obtained in its decomposition could be identified. According as a salicylic or a benzoic derivative was obtained in any given decomposition of the compound, there was the certainty that the percentage of that portion of the molecule must be ascribed to the aldehyde on the one hand, or to the diketone on the other.

Action of Salicylaldehyde and Ammonia on Benzil.

Equal weights of salicylaldehyde and benzil were dissolved in alcohol with the aid of heat, and the warm solution was saturated with gaseous ammonia. During the process the new compound

separated as a lemon-yellow crystalline powder. In order to prevent the delivery-tube from being choked by the solid substance, the ammonia was passed into the liquid through a wide T-piece, one end of the cross-limb of which was closed by a perforated cork, whilst the other was immersed in the liquid. A glass rod, working air-tight through the cork, served to clear the tube without interrupting the operation.

The saturated liquid was allowed to stand for some hours, after which the substance was filtered off and extracted two or three times with boiling alcohol, in which it is practically insoluble. In this condition it was employed for the various reactions about to be described, although it still retained its yellow color. The yield in various operations was very constant, and amounted to about three-fourths of the united weights of the benzil and salicylaldehyde employed.

For analysis a portion was further purified by dissolving it in boiling phenol and precipitating with alcohol, repeating these operations. It was thus obtained as a white crystalline sandy powder, consisting of microscopic plates. When heated in a capillary tube it becomes dark-colored at about 260°, and fuses with decomposition above 300°. It is almost insoluble in alcohol, ether, glacial acetic acid, and the other ordinary organic solvents. Boiling phenol dissolves it most readily.

Analysis gave figures agreeing with the formula $C_{28}H_{24}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1190	0.3237	0.0582
II.	0.1678	0.4550	0.0844

III. 0.1140 gram burnt with copper oxide in a vacuum gave 6.1 cc. moist nitrogen at 14° and under 761 mm. pressure.

	Calculated for $C_{28}H_{24}N_2O_4$.		Found.		
			I.	II.	III.
C_{28}	336	74.34	74.19	73.95	...
H_{24}	24	5.31	5.43	5.59	...
N_2	28	6.19	...	...	6.30
O_4	64	14.16	...	...	...
	452	100.000			

The equation according to which this compound is formed has already been given.

It is remarkable that in the case of parahydroxybenzaldehyde the reaction with benzil ammonia takes place according to equation II, yielding parahydroxylophine,[1] whereas, when the isomeric salicylaldehyde is substituted for the para-compound, the reaction takes place as above according to equation III.

Action of Caustic Soda on the Condensation Product.—The compound dissolves in caustic soda. The solution was boiled for several days, at the end of which time nearly the whole of the substance was precipitated unchanged on the addition of hydrochloric acid. Some slight decomposition had, however, taken place, as a small quantity of benzoic acid could be extracted from the acidified liquid by treatment with ether, but no salicylic acid could be detected.

By fusion with caustic soda the substance yields benzoic and salicylic acids. The former was identified by its fusion point, the latter by the violet coloration with ferric chloride.

Action of Hydrochloric Acid on the Condensation Product.—By heating the compound with dilute hydrochloric acid (fuming acid diluted with twice its volume of water) at a temperature of 210° in sealed tubes for five hours, the benzil portion of the molecule is removed as benzoic acid and the hydrochloride of a new base is obtained. When a more concentrated acid or a higher temperature is employed, the benzoic acid is obtained as before, but the base is resinised, whilst at a somewhat lower temperature no action takes place. A large excess of the aqueous acid must be used, as any substance which is not in solution during the reaction is resinised. Even under the most favorable conditions it was found impossible to prevent entirely the formation of resin.

On warming the liquid thus obtained, the benzoic acid and the hydrochloride went into solution, whilst the resin, together with any unaltered substance, remained undissolved. The base, precipitated from the filtered solution by the addition of ammonia, was contaminated with resin. It was dissolved in an excess of hot benzene, and on cooling the liquid deposited the greater part of the resin. The filtered solution, which was only slightly colored, was evaporated to a small bulk, and, on cooling, yielded the base in a crystalline form. The substance was recrystallised from benzene until the constant fusing point 180.5° was obtained. It is readily soluble in hot benzene, almost insoluble in the cold. It is

[1] Chem. Soc. Jour. 1882, **1**, 326.

deposited from the benzene solution in groups of small lustrous laminæ, which are soluble in alcohol, ether and chloroform. Water dissolves it very slightly, but it is soluble in caustic alkalis.

Analysis gave numbers pointing to the formula $C_{14}H_{16}N_2O_2$.

	Substance.	CO_2.	OH_2.
I.	0.1282	0.3229	0.0764
II.	0.1226	0.3084	0.0735

III. 0.0991 gram burnt with copper oxide in a vacuum gave 10.05 cc. moist nitrogen at 20.3° and under 762.8 mm. pressure.

	Calculated for $C_{14}H_{16}N_2O_2$.		Found.		
			I.	II.	III.
C_{14}	168	68.85	68.69	68.60	...
H_{16}	16	6.56	6.62	6.66	...
N_2	28	11.48	...	...	11.62
O_2	32	13.11	...	...	...
	244	100.00			

This base is formed from the original compound according to the equation—

$$C_{28}H_{24}N_2O_4 + 2OH_2 = \underset{\text{Base.}}{C_{14}H_{16}N_2O_2} + 2\underset{\text{Benzoic acid.}}{C_7H_6O_2}.$$

We shall show later that the original condensation product is a dibenzoyl-derivative of this base.

The preparation of any considerable quantity of the base by the foregoing method is a matter of great difficulty, but farther on a method will be described by which the base can be obtained with relative ease. The salts were prepared from a specimen of base obtained by this second method.

The *platinichloride* is deposited in large transparent orange-colored crystals, consisting of thick rhomboidal plates with bevelled edges, when platinic chloride is added in excess to a solution of the hydrochloride and the liquid is evaporated over sulphuric acid. The presence of an excess of hydrochloric acid is to be avoided, as it causes the salt to be contaminated with hydrochloride, which is less soluble in the concentrated acid than the platinichloride. The crystals contain water of crystallisation. They are permanent in air, but effloresce over sulphuric acid and become anhydrous at 100°.

0.5026 gram crystallised salt lost on heating to 100° 0.0501 gram.

	Calculated for $C_{14}H_{16}N_2O_2$, $2HClPt$, Cl_4, $4OH_2$	Found.
Water in 100 parts	9.89	9.97

0.2134 gram anhydrous salt left on ignition 0.0638 gram platinum.

	Calculated for $C_{14}H_{16}N_2O_2$, $2HCl$, $PtCl_4$.	Found.
Pt in 100 parts	30.03	29.90

The *hydrochloride* is obtained as a crystalline powder, consisting of microscopic plates, when concentrated hydrochloric acid is added to a saturated solution of the base in dilute hydrochloric acid. It has a pungent, bitter taste, perceptible even with very dilute solutions.

The normal *sulphate* crystallises in prisms, very soluble both in water and in alcohol.

The *picrate* is precipitated in microscopic needles when an aqueous solution of picric acid is added to the solution of a salt of the base. It is practically insoluble in cold water, and dissolves only very slightly on boiling.

When fused with caustic soda the base yields salicylic acid as sole organic product.

As regards the constitution of this base, it is evident from its mode of formation (see equation) that it contains the whole of the salicylic portion of the molecule of the original compound. It therefore contains the group $(C.C_6H_4.OH)'''$ twice, and may be formulated $(C.C_6H_4.OH)_2N_2H_6$. It is very improbable that in the processes in which this compound has been formed a union of the nitrogen-atoms with each other can have occurred; and the only alternative is to assume a union of the salicylic complexes, in which case the compound would have the formula—

$$\begin{array}{l} C_6H_4(OH).CH.NH_2 \\ \quad\quad\quad\quad\quad | \\ C_6H_4(OH).CH.NH_2. \end{array}$$

A compound of this constitution might be designated *dihydroxystilbenodiamine*, a name constructed on the analogy of *ethylenediamine*.

The above formula accounts for the diacid character of the base, for its solubility in caustic alkalis, for the fact that it yields salicylic acid by fusion with caustic soda, and for the formation of the various compounds described farther on.

We sought for confirmation of this constitution in the action of nitrous acid on the compound. On adding a dilute solution of sodic nitrate to an acidulated solution of the base, gas was evolved and a neutral body separated, which, by crystallisation from benzene, was obtained in colorless microscopic octohedra. The quantity was unfortunately too small for further examination, the greater part of the base being resinised in the process. The failure was possibly due to the presence of the hydroxyl-groups; by the action of hydriodic acid, however, it may be possible to convert the base into the non-hydroxylated compound, stilbene-diamine, and this with nitrous acid may possibly yield hydro-benzoin, thus definitively proving the constitution of the compound. These reactions will be studied by one of us as soon as the base has been obtained in sufficient quantity.

A systematic study of the reactions of the base, as compared with those of the orthodiamines of the benzene series, will also be undertaken. The base, as containing two amido-groups attached to contiguous carbon-atoms of a fatty chain, is a fatty analogue of an orthodiamine. It will be of special interest to ascertain whether the characteristic condensations in the ortho-series, of diamines with acids, aldehydes, etc., occur in the case of this compound. The analogy between benzene compounds of the ortho-series and certain fatty compounds, an analogy exemplified in the case of the phthalic and succinic compounds, of phthalide and the γ-lactones, of the anhydro-bases and glyoxaline, and in many other cases, points to a possibility of the occurrence of such reactions.

Action of Acetic Anhydride on the Condensation Product.—A quantity of the condensation product was boiled with twice its weight of acetic anhydride until the whole had dissolved, a process which required about six hours for completion. As soon as this happens, the boiling must be interrupted, since by the continued action of the anhydride the derivative first produced undergoes a further transformation, yielding a compound to be described further on. On cooling, the new substance separated from the dark solution in colorless rhomboidal laminæ. These were washed with alcohol and recrystallised from boiling acetic acid, from which they were deposited in the foregoing forms. The substance melted at 225–227°. The melting point was not altered by further recrystallisation. This compound is only sparingly soluble in boiling alcohol, separating in thin rhomboidal lustrous laminæ.

Analysis gave figures pointing to a diacetyl-derivative,

$C_{28}H_{22}(C_2H_3O)_2N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1120	0.2929	0.0527
II.	0.1258	0.3288	0.0601

III. 0.1776 gram burnt with copper oxide in a vacuum gave 8.35 cc. moist nitrogen at 23.5° and under 759.5 mm. pressure.

	Calculated for $C_{28}H_{22}(C_2H_3O)_2N_2O_4$.		Found.		
			I.	II.	III.
C_{32}	384	71.64	71.32	71.28	...
H_{26}	28	5.22	5.23	5.31	...
N_2	28	5.22	...	...	5.28
O_4	96	17.92	...	...	...
	536	100.00			

Hot dilute caustic potash dissolved the compound, at the same time removing the acetyl-groups; hydrochloric acid added to this solution precipitated the original condensation product.

The acetic anhydride mother-liquor from the diacetyl-derivative contained benzoic acid (or benzoic anhydride) derived from the decomposition of a portion of the substance, and also a mixture of compounds sparingly soluble in alcohol. We could not succeed in separating these last from one another. By long boiling with acetic anhydride they are converted into the compound described in the following paragraph.

By continuing the boiling of the condensation product with acetic anhydride for about eight hours after the whole of the substance had passed into solution, a totally different compound was obtained. On cooling, the dark-colored liquid deposited a crystalline substance, which was washed with acetic acid and then recrystallised from this solvent until the melting point remained constant. It was thus obtained in thin colorless prismatic crystals containing acetic acid. After expelling the acetic acid by heating at 130° the compound melted at 216–219°. The yield was about two-fifths of the weight of the condensation product taken. Analysis of the substance dried at 130° gave figures agreeing with the formula $C_{28}H_{14}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1391	0.3254	0.0757
II.	0.1223	0.2855	0.0647

III. 0.1338 gram burnt with copper oxide in a vacuum gave 8.76 cc, moist nitrogen at 28.7° and under 755 mm. pressure.

	Calculated for $C_{22}H_{24}N_2O_4$.		Found.		
			I.	II.	III.
C_{22}	264	64.08	63.80	63.67	...
H_{24}	24	5.82	6.05	5.88	...
N_2	28	6.80	...	...	7.10
O_4	96	23.30	...	...	...
	412	100.00			

The compound dissolves readily in hot alcohol, and, on cooling, is deposited in thin colorless prisms containing 1 mol. of alcohol of crystallisation.

1.5322 grams of the substance, crystallised from alcohol and air-dried, lost on heating at 120° 0.1496 gram.

	Calculated for $C_{22}H_{24}N_2O_4$, C_2H_6O.	Found.
Alcohol in 100 parts,	10.04	9.76

We further satisfied ourselves that the compound $C_{22}H_{24}N_2O_3$ is formed from the pure diacetyl compound by long boiling with acetic anhydride. It may also be readily obtained by heating the original condensation product with acetic anhydride in a sealed tube at 150° for about four hours. At this higher temperature the transformation is very complete.

The acetic anhydride mother-liquor, which remained after the separation of the compound $C_{22}H_{24}N_2O_6$, contains large quantities of benzoic acid (or benzoic anhydride). After expelling the excess of acetic anhydride, the residue dissolved almost completely in boiling sodic carbonate, and, on adding hydrochloric acid, the benzoic acid was precipitated. It was identified by its fusing point and other characteristic properties.

The formation of the compound $C_{22}H_{24}N_2O_6$ from the original condensation product may be accounted for as follows: In the first place the diacetyl-derivative is formed; this is then further acted on by acetic anhydride according to the equation—

$$\underset{\text{Diacetyl-derivative.}}{C_{28}H_{22}(C_2H_3O)N_2O_4} + \underset{\text{Acetic anhydride.}}{\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\!\!>\!O} = \underset{\text{Second acetyl-derivative.}}{C_{22}H_{24}N_2O_6} + \underset{\text{Benzoic anhydride.}}{\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}\!\!>\!O}.$$

The simplest interpretation of this reaction would be that two benzoyl-groups in the diacetyl-derivative have been replaced by two acetyl-groups. If we, therefore, formulate the compound $C_{22}H_{24}N_2O_6$ as a tetracetyl compound, thus:

$$C_{14}H_{12}(C_2H_3O)_4N_2O_2,$$

it appears as a tetracetyl-derivative of a compound $C_{14}H_{16}N_2O_2$. This is, however, the formula of *dihydroxystilbenediamine*. The reactions of the compound $C_{22}H_{24}N_2O_6$, which we are about to describe, show it to be *diacetyl-diacetoxystilbenediamine*:

$$C_6H_4(O.C_2H_3O).CH.NH(C_2H_3O)$$
$$|$$
$$C_6H_3(O.C_2H_3O).CH.NH(C_2H_3O).$$

As, according to the above view, the whole of the benzil portion of the original molecule has been removed in the formation of this compound, it appeared important to show that no benzoic acid is obtained from the compound by oxidation. A portion was heated with potassium permanganate in akaline solution as long as the color of the permanganate was discharged. Not a trace of benzoic acid was obtained. The diacetyl-derivative of the condensation product, treated in the same way, yielded large quantities of benzoic acid.

Action of Caustic Alkali on the Compound $C_{22}H_{24}N_2O_6$.—8 grams of the compound were boiled for a few minutes with a solution of 15 grams of potash in 75 cc. of water; it readily dissolved, and, on adding hydrochloric acid, a white substance was precipitated. This was filtered off, washed with water, boiled with alcohol, in which it is practically insoluble, and, after drying, was dissolved in hot phenol, and precipitated from the solution with alcohol. The crystallisation from phenol was repeated. In this way the substance was obtained as a white crystalline powder melting above 300°.

Analysis gave figures agreeing with the formula $C_{18}H_{20}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1262	0.3042	0.0714
II.	0.1353	0.3263	0.0755

III. 0.1462 gram burnt with copper oxide in a vacuum gave 10.3 cc. moist nitrogen at 19° and under 768.8 mm. pressure.

	Calculated for $C_{18}H_{20}N_2O_4$.—		Found.		
			I.	II.	III.
C_{18}	216	65.85	65.74	65.78	...
H_{20}	20	6.10	6.29	6.20	...
N_2	28	8.54	...	...	8.19
O_4	64	19.51	...	...	...
	328	100.00			

The action of the potash had, therefore, been to remove two acetyl-groups. These must be the two acetyl-groups attached to oxygen, as their removal constitutes the condition of the solubility of the compound in alkalis. The new compound would thus be *diacetyldihydroxystilbenediamine*, and would possess the constitution—

$$C_6H_4(OH).CH.NH(C_2H_3O)$$
$$|$$
$$C_6H_4(OH).CH.NH(C_2H_3O).$$

We show later on that the original condensation-product, which in its physical properties (high fusing point, sparing solubility, etc.) closely resembles the present compound, is the corresponding dibenzoyl-derivative of the base—*dibenzoyldihydroxystilbenediamine*.

By boiling the compound $C_{22}H_{24}N_2O_6$ with strong potash for an hour, all four acetyl-groups were removed, and the base dihydroxystilbenediamine was formed. This was separated by acidifying the solution with hydrochloric acid and then precipitating with ammonia. A considerable quantity of resin was formed by the action of the strong potash, which rendered the purification of the base a matter of difficulty. For this reason the melting point was found too low—175° instead of 180.5°. A microscopic examination of the crystals showed that they had exactly the same forms as those of the base already described. All doubt as to the identity of the two products is dispelled by the result of the action of hydrochloric acid on the compound $C_{22}H_{24}N_2O_6$, a reaction in which the base can readily be obtained in a state of purity.

Action of Hydrochloric Acid on the Compound $C_{22}H_{24}N_2O_6$.—Fuming hydrochloric acid dissolved the compound in the cold. On standing, and more rapidly on heating, the solution deposited a white crystalline substance. The physical properties of this pointed to its identity with diacetyldihydroxystilbenediamine, the compound obtained by the foregoing action of dilute potash. The

substance, after being dissolved in phenol and precipitated with alcohol, yielded on analysis figures agreeing with the required formula $C_{18}H_{20}N_2O_4$. (Percentages: calculated, C = 65.85, H = 6.09; found, C = 65.66, H = 6.23.)

By heating the compound $C_{22}H_{24}N_2O_6$ for three hours with concentrated hydrochloric acid in sealed tubes at 120°, the four acetyl-groups were removed and dihydroxystilbenediamine was obtained. On cooling, the tube contained large crystals of the hydrochloride. This method of preparing the base gives much better results than the direct decomposition of the original condensation compound with hydrochloric acid. In practice the compound $C_{28}H_{24}N_2O_6$ yields about half its weight of pure base. The base, liberated from the hydrochloride by ammonia, was purified as before by crystallisation from benzene.

The material employed in the various experiments, and in the preparation of the salts of the base, was prepared by the foregoing method.

Action of Benzoic Anhydride on the Condensation Product.—A quantity of the compound was heated with excess of benzoic anhydride until the whole had liquefied. The cooled product of the reaction was treated with alcohol, to remove benzoic anhydride and benzoic acid. The undissolved portion was recrystallised from acetic acid, and was thus obtained in colorless microscopic plates, which melted at 246–248°.

Analysis gave figures agreeing with the formula of a dibenzoyl-derivative, $C_{28}H_{22}(C_7H_6O)_2N_2O_4$:

	Substance.	CO_2.	OH_2.
I.	0.1656	0.4607	0.0734
II.	0.1490	0.4151	0.0664

III. 0.1882 gram burnt with copper oxide in a vacuum gave 7.1 cc. moist nitrogen at 22.7° and 765.5 mm. pressure.

	Calculated for $C_{28}H_{22}(C_7H_6O)_2N_2O_4$.		Found.		
			I.	II.	III.
C_{42}	504	76.36	75.87	75.98	...
H_{32}	32	4.85	4.92	4.95	...
N_2	28	4.24	...	...	4.29
O_6	96	14.55	...	...	...
	660	100.00			

As it was important, from the point of view of the proof of the constitution of the condensation product which we are about to give, to show that no rearrangement of the atoms of the original molecule had taken place during the formation of this dibenzoyl-derivative, beyond the introduction of the benzoyl-groups, we converted this derivative back into the condensation product. This was accomplished by boiling the compound with dilute caustic potash (1 part of caustic potash dissolved in 8 parts of water) until nearly the whole had passed into solution, a process which required several hours. From the filtered liquid, hydrochloric acid precipitated a white substance, which, after crystallisation from phenol, had all the physical properties of the original condensation product, and yielded on analysis figures agreeing with the required formula, $C_{28}H_{24}N_2O_4$. (Percentages: calculated, C = 74·33, H = 5·31; found, C = 74·54, H = 5·49.)

Action of Acetic and Benzoic Anhydrides on Dihydroxystilbenediamine.—In the foregoing pages we have regarded the original condensation product, and a number of the compounds obtained from it, as derived from the base dihydroxystilbenediamine by the replacement of hydrogen by acid radicals. The facts adduced in support of this view have been chiefly analytical.

The experiments about to be described furnish confirmatory evidence by the synthetic production of these compounds from the base.

A portion of the base was treated with acetic anhydride in the cold. A reaction immediately took place, with development of heat, and a very difficultly soluble white compound was formed, which by its physical properties was recognised as diacetyldihydroxystilbenediamine.

A fresh quantity of the base was heated in a sealed tube with acetic anhydride for several hours at 150°. In this way diacetyldiacetoxystilbenediamine was obtained. It was deposited from its hot alcoholic solution in the characteristic thin colorless prisms, which, after heating to expel the alcohol of crystallisation, melted at 216–219°.

A quantity of the base was heated with benzoic anhydride. At first the whole fused; then, almost immediately, a difficultly fusible substance separated. This was in all probability the original condensation-product, which had thus been regenerated; but, as the quantity of base at our disposal was limited, we preferred to

carry the reaction further and obtain the dibenzoyl-derivative of the condensation-product, which can be more readily purified than the condensation-product itself. The heating was, therefore, continued until the whole had again fused, after which the operation was interrupted. The product of the reaction was treated with alcohol, and the insoluble portion was crystallised from acetic acid. The compound was thus obtained in microscopic plates indistinguishable from those of the dibenzoyl-derivative of the condensation-product, and, like these, melting at 246–248°.

The dibenzoyl-derivative of the condensation-product,

$$C_{28}H_{20}(C_7H_5O_2)_2N_2O_4,$$

is, therefore, identical with the tetrabenzoyl-derivative of the base. It would thus have the formula—

$$\begin{array}{l} C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O) \\ \qquad\qquad\qquad\qquad\quad | \\ C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O). \end{array}$$

We have already shown that this compound may be converted into the condensation-product by boiling it with potash, two benzoyl-groups being removed in the process. Thus the synthesis of this product from the base has been accomplished. As the condensation-product is soluble in caustic alkalis, the two benzoyl-groups which are thus removed must be those which are attached to oxygen in the above compound. The condensation-product is, therefore, *dibenzoyldihydroxystilbenediamine*, and its formation from salicylaldehyde, benzil, and ammonia may be represented thus:

$$2C_6H_4(OH).CHO + \begin{array}{l} CO.C_6H_5 \\ | \\ CO.C_6H_5 \end{array} + 2NH_3 =$$

$$\begin{array}{l} C_6H_4(OH).CH.NH.CO.C_6H_5 \\ \qquad\qquad\quad | \\ C_6H_4(OH).CH.NH.CO.C_6H_5 \end{array} + 2OH_2.$$

Dibenzoyldihydroxystilbenediamine.

Action of Furfuraldehyde and Ammonia on Benzil.—20 grams of benzil together with 18 grams of furfuraldehyde were dissolved in alcohol, and the liquid was saturated with gaseous ammonia, conducting the operation as already described (pp. 2 and 3). At first a heavy granular white powder separated, but, when the saturation was nearly complete, the liquid became filled with a bulky substance,

differing in appearance from the first. After standing for some hours the mixture of substances was filtered off and boiled with alcohol, which dissolved only the bulky substance. The granular substance, which resembled in its properties the compound obtained with salicylaldehyde, was purified by dissolving it in hot phenol and precipitating with alcohol. It was deposited as a crystalline powder. It is practically insoluble in most of the ordinary solvents, but boiling glacial acetic dissolves it slightly. The melting point lies above 300°.

Analysis gave figures agreeing with the formula $C_{24}H_{20}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1518	0.3989	0.0694
II.	0.1526	0.3301	0.0586

III. 0.1943 gram burnt with copper oxide in a vacuum gave 12.2 cc. moist nitrogen at 18.5° and under 757 mm. pressure.

	Calculated for $C_{24}H_{20}N_2O_4$.		Found.		
			I.	II.	III.
C_{24}	288	72.00	71.67	71.68	...
H_{20}	20	5.00	5.08	5.19	...
N_2	28	7.00	...	...	7.20
O_4	64	16.00	...	...	...
	400	100.00			

The following equation, which exactly corresponds with that in which the compound from salicylaldehyde is formed, expresses the reaction:

$$\underset{\text{Benzil.}}{C_{14}H_{10}O_2} + 2\underset{\text{Furfuraldehyde.}}{C_5H_4O_2} + 2NH_3 = \underset{\text{New compound.}}{C_{24}H_2N_{20}O_4} + 2OH_2.$$

The second compound formed in the above process was purified by recrystallisation from alcohol until the melting point remained constant. It was deposited from its solution in boiling alcohol in tufts of silky needles melting at 246°. Analysis showed that this compound possessed the same percentage composition as the foregoing.

	Substance.	CO_2.	OH_2.
I.	0.1163	0.3061	0.0533

II. 0.1328 gram burnt with copper oxide in a vacuum gave 8.8 cc. moist nitrogen at 21.3° and under 752.5 mm. pressure.

	Calculated for $C_{24}H_{20}N_2O_4$.		Found.	
			I.	II.
C_{24}	288	72.00	71.78	...
H_{20}	20	5.00	5.09	...
N_2	28	7.00	...	7.45
O_4	64	16.00	...	...
	400	100.00		

We have as yet made no experiments to ascertain the nature of this isomerism.

The study of these reactions, including those of dihydroxystilbenediamine already indicated, will be continued.

NORMAL SCHOOL OF SCIENCE,
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ON CONDENSATION COMPOUNDS OF BENZIL WITH ETHYL ALCOHOL.[1]

BY MARY E. OWENS AND FRANCIS R. JAPP.

In preparing benzilic acid by heating benzil with alcohol potash, Jena[2] observed the formation of a neutral compound, melting at 200°, to which he ascribed the formula $C_{14}H_{12}O_2$, regarding it as isomeric with benzoïn. He assigned to it the name *tolane alcohol.* The quantity at his disposal was insufficient for further investigation.

Limpricht and Schwanert[3] obtained the same compound by heating together benzoïn and alcoholic potash with access of air. They arrive at the conclusion that it is a derivative of benzoïn (although they show in the same experiment that benzil is formed under the above conditions by the oxidising action of the air upon the benzoïn), and state their suspicion that the benzil employed by Jena must have contained benzoïn. On the strength of their analyses (not published) they arrive at the formula $C_{30}H_{26}O_4$, and name the compound *ethyldibenzoïn.*

We have found that, by the protracted action of very dilute alcoholic potash upon benzil in the cold, the above compound is

[1] Communicated by the authors. [2] Liebig's Annalen **155**, 79.
[3] Ber. d. deutsch. chem. Ges. **4**, 335.

formed in large quantity. The yield, amounting in one experiment to 6 grams from 10 grams of carefully purified benzil, quite precludes the possibility of a formation from benzoïn present as an impurity. Our analyses lead to the formula $C_{30}H_{24}O_4$, which differs from that of Limpricht and Schwanert by containing two atoms of hydrogen fewer. The formation of such a compound from benzil and alcohol might be expressed by the equation

$$2C_{14}H_{10}O_2 + C_2H_6O = C_{30}H_{24}O_4 + OH_2.$$

In order to prepare this compound, 10 grams of caustic potash were dissolved in 2½ litres of alcohol, and to the solution thus obtained 200 grams of finely powdered benzil were added. The whole was shaken until the liquid was saturated with benzil, after which it was allowed to stand, shaking from time to time. The separation of the compound begins at the end of the first or second day, and is practically complete in about a fortnight. It is thus obtained as a crystalline powder, but when a larger quantity of alcohol is employed, so as to have all the benzil in solution from the commencement, it separates in moderately large lustrous crystals.

The crude substance was washed with ether to remove unaltered benzil, and then recrystallised, first from benzene, and afterwards from alcohol. The latter solvent deposits the compound in small lustrous crystals. These contain alcohol of crystallisation, which they lose only after long heating at 120°. At 100° they are permanent. The compound thus freed from alcohol melted at 200–201°, and yielded on analysis numbers agreeing with the formula $C_{30}H_{24}O_4$. We append, for the sake of comparison, the theory for Limpricht and Schwanert's formula $C_{30}H_{26}O_4$:

	Substance.	CO_2.	OH_2.
I.	0.1258	0.3694	0.0612
II.	0.1448	0.4260	0.0702

	Calculated for $C_{30}H_{24}O_4$. (Owens and Jappˑ)	Calculated for $C_{30}H_{26}O_4$. (Limpricht and Schwanert.)	Found. I.	Found. II.
C	80.36	80.00	80.08	80.24
H	5.36	5.78	5.41	5.38
O	14.28	14.22	...	...
	100.00	100.00		

The difference in the percentages required by the two formulæ is certainly rather small for analysis alone to decide between them,

but we think that the mode of formation which we have just described renders the first formula the more probable. Further, if the second formula was correct, the errors of analysis, both for carbon and hydrogen, would be in the wrong direction, whereas with the first formula the errors are in the usual direction.

We think that the results obtained by our predecessors are possibly due to their having overlooked the alcohol of crystallisation, or, at all events, to their not having taken into account the difficulty of completely expelling this alcohol. They crystallised the substance from alcohol, but none of them mention the presence of alcohol of crystallisation. Jena appears to have analysed a compound from which only a portion of the alcohol had been expelled. Thus, the formula $C_{30}H_{24}O_4,C_2H_6O$ requires C 77·73 and H 6.07 per cent., whilst Jena finds C 78.7 and H 5.8 per cent., or values intermediate between the foregoing and those required for the formula $C_{30}H_{24}O_4$. A similar, though smaller, error may have lowered the carbon and raised the hydrogen in Limpricht and Schwanert's analyses. The melting point of the substance analysed would probably afford no intimation of the presence of the alcohol, for we have found that the crystals containing alcohol do not, unless the temperature is rapidly raised in determining the melting point, melt lower than those from which the alcohol has been previously expelled.

A determination of alcohol of crystallisation was made, with the following result:

1.3890 gram of crystallised substance lost on heating at 120° 0.1284 gram.

	Calculated for $C_{30}H_{24}O_4,C_2H_6O$.	Found.
Alcohol in 100 parts,	9.31	9.24

As the percentage of hydrogen in the compound $C_{30}H_{24}O_4,C_2H_6O$ differs from that of a compound of the formula $C_{30}H_{26}O_4,C_2H_6O$, we analysed a specimen of the air-dried substance containing alcohol of crystallisation:

Substance	CO_2.	OH_2.
0.1145	0.3256	0.0619

	Calculated for $C_{30}H_{24}O_4,C_2H_6O$.		Found.
C_{32}	384	77·73	77·55
H_{30}	30	6.07	6.01
O_5	80	16.20	...
	494	100.00	

The formula $C_{30}H_{26}O_4,C_6H_6O$, on the other hand, requires C 77.42 and H 6.45 per cent. The value obtained for hydrogen, coupled with that yielded by the compound dried at 120°, appears to us to afford strong evidence in favor of the formula with less hydrogen.

From a solution in hot benzene, the condensation-product is deposited in minute rhomboidal plates, generally grouped in rosettes, and containing benzene of crystallisation. The crystals effloresce when exposed to the air and become opaque. A portion of the crystallised substance, freed from adhering benzene by pressure between filter-paper and brief exposure to the air, lost, on heating at 120°, 14.96 per cent. of its weight. The formula $C_{30}H_{24}O_4,C_6H_6$ requires a loss of 14.83 per cent.

Limpricht and Schwanert[1] state that by heating "ethyldibenzoïn" with acetyl chloride a monacetyl-derivative melting at 145° is obtained. We have been unable to confirm this result. The substance may be heated for an hour with acetyl chloride at 100° without undergoing change. Protracted heating, or a higher temperature, produces resination. We were equally unable to obtain an acetyl-derivative by boiling the substance with acetic anhydride. We have, however, made an observation which, we think, explains the supposed existence of a monacetyl-derivative. When the condensation-product is recrystallised several times from glacial acetic acid, the melting point sinks each time until a limit is reached, when a substance is obtained melting at about 130°. This limit may be reached in a single crystallisation, by boiling the compound for some hours with the acetic acid. The substance thus obtained is not an acetyl-derivative, but a compound of the condensation-product with acetic acid (or possibly with acetyl and hydroxyl). On exposure to the air, and more rapidly on heating, it parts with acetic acid; and its melting point lies anywhere between 130° and 200° (the melting point of the original substance), according to the amount of drying to which it has been subjected. It is possible that Limpricht and Schwanert, if they employed acetic acid as a solvent, may have obtained this molecular compound, and analysed a product from which the acetic acid had been only partially expelled. This would account for the melting point found by these investigators; and the substance in this condition would also give figures agreeing more or less closely with those required for a monacetyl-derivative, seeing that the composition of such a

[1] *Loc. cit.*

derivative lies almost intermediate between that of the molecular compound and that of the original condensation-product.

	Calculated for		
	$C_{30}H_{24}O_4,C_2H_4O_2$.	$C_{30}H_{23}(C_2H_3O)O_4$.	$C_{30}H_{24}O_4$.
C	75·59	78·37	80·36
H	5·51	5·31	5·36
O	18·90	16·32	14·28
	100·00	100·00	100·00

A specimen of the molecular compound, melting at 133°, gave on analysis C 75·48 and H 5·34 per cent.

As Limpricht and Schwanert publish no details of preparation, or analytical figures, in connection with their acetyl compound, we have no means of testing the correctness of the above supposition.

In the benzene mother-liquors remaining from the purification of the foregoing condensation-product we found a second substance, which was deposited in minute yellow crystals melting at 232°. A larger quantity of this substance was obtained from the original alcoholic potash mother-liquors (after removing the compound $C_{30}H_{24}O_4$) by acidifying with hydrochloric acid, distilling off the alcohol to a small bulk, and precipitating the organic substance by the addition of water. This precipitated substance was treated with alcohol, in order to remove benzoic acid and a soluble resin, and the crystalline residue was dissolved in hot phenol and reprecipitated with alcohol. By a repetition of this crystallisation from phenol, the substance was obtained as a yellow crystalline powder, melting as above at 232°. Analysis gave numbers agreeing with the formula $C_{46}H_{34}O_4$:

	Substance.	CO_2.	OH_2.
I.	0·1354	0·4204	0·0657
II.	0·1534	0·4769	0·0742
III.	0·1492	0·4640	0·0735

	Calculated for $C_{46}H_{34}O_4$.		Found.		
			I.	II.	III.
C_{46}	552	84·92	84·67	84·78	84·81
H_{34}	34	5·23	5·39	5·37	5·47
O_4	64	9·85	...	...	...
	650	100·00			

These analyses were made with different preparations.

The formation of a compound of the above formula from benzil and alcohol may be expressed by the following equation:

$$3C_{14}H_{10}O_2 + 2C_2H_6O = C_{46}H_{34}O_4 + 4OH_2.$$

We have also found that dilute alcoholic potash acts slowly upon benzoïn in the cold, and, when air is excluded during the reaction, gradually converts it into a compound crystallising in silky needles, which melt at 250° and are apparently distinct from any of the compounds hitherto obtained by the action of potash upon benzoïn. An account of this reaction is reserved for a future communication.

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ON A SCHEME FOR THE QUALITATIVE DETERMINATION OF THE BASES WITHOUT HYDROGEN SULPHIDE.

BY GEORGE S. EYSTER.

There are many technical laboratories fitted for special work where an extended qualitative examination is seldom made. If a sulphuretted hydrogen apparatus is at hand it is out of order, and to put it in working condition often requires more time than the assay. On the other hand, sulphydric acid solution keeps badly and is inconvenient to use from want of strength. Strong solution of ammonium sulphide can now be had from the dealers in chemicals, and if preserved in a closet, its keeping powers are satisfactory. It is much stronger than solution of sulphydric acid, and in many cases time can be saved by its use.

While the following scheme is not proposed as a complete substitute for the ordinary course of analysis in a well-equipped laboratory, yet from the experiments of the writer, he thinks its employment will, in most cases, be satisfactory to a careful analyst. It is intended especially for use in situations where hydrogen sulphide is not so available, and where, as in travelling, compactness in apparatus and materials is desirable.

The scheme is given in rather an extended shape, so that those who may wish to give it a trial will have all the main points at hand. Zettnow's scheme has been followed to some extent in the use of sulphuric acid as a separating reagent. Attention is called to some points, in the notes, that would not so readily occur to one accustomed only to the ordinary procedure. It is hoped that the remaining precautions are such as would occur to any chemist. The old expressions, soda, potassa, ammonia (solution understood), are retained for brevity.

My thanks are due Prof. E. S. Breidenbaugh for facilities afforded me in the Chemical Laboratory of Pennsylvania College for the prosecution of necessary experiments in the testing of the following scheme.

Some of the rarer elements more likely to occur in ordinary work are merely indicated.

(The solution has a neutral or acid reaction.)

I. (Ag, Pb, Hg)

Add dilute hydrochloric acid, filter, wash. Precipitate 1, Filtrate II.

1. Wash with hot water, add H_2SO_4 to washings. *White precipitate*, Lead.

2. Pour ammonia over residue from 1;

   a. Residue *blackens*, Mercury.

   b. Acidify filtrate from 1 with HNO_3. *White precipitate*, Silver.

II.[1] (Ba, Sr, Ca, Pb)

Add dilute sulphuric acid. Precipitate 1, Filtrate III.

1. Boil with sodium carbonate, filter, wash, dissolve in hydrochloric acid.

2[2]. Add ammonia and ammonia sulphide. *Black precipitate*, Lead.

3[3]. Evaporate to dryness with HCl filtrate from 2, treat residue with strong alcohol, filter. Examine Residue 4, Filtrate 5.

4. Test with flame reaction for *Barium*.

5. Add equal bulk water and a few drops hydrofluosilic acid, allow to stand, filter (Ba), add H_2SO_4, filter, wash with weak alcohol, boil with Na_2CO_3 and convert into chlorides (see 1 and 3),

add to solution potassium sulphate,[1] allow to stand. *White precipitate*, Strontium.

6. Add ammonia and oxalate of ammonium to filtrate from 5; allow to stand in warm place. *White precipitate*, Calcium.

III. (Hg, Pb, Bi, Cd, Cu, Co, Ni)

If the color indicates much *chromic acid*, boil with hydrochloric acid and a few drops alcohol until all the chromic acid is reduced, then, if enough HCl is not present, add NH_4Cl, and—

A. Add ammonia and ammonium sulphide, both in slight excess, heat, agitate, filter, wash. Precipitate *B*, Filtrate IV.

B[a]. Treat with ammonium sulphide in excess (if Cu be present, boil, or use sodium sulphide), filter, wash with water containing a little $(NH_4)_2S$. Residue *C*, Filtrate IV.

C. Treat with dilute HCl, filter, wash. Residue *D*, Filtrate V.

D. Boil with dilute HNO_3, filter, wash. Residue 1, Filtrate 2.

1. *Black residue*,[2] Mercury. *Test with* Na_2CO_3 *in glass tube.*

2[b]. Drive off excess acid, add dilute H_2SO_4. *White precipitate*, Lead.

3. To filtrate from 2 add ammonia. *White precipitate*, Bismuth.

4. Evaporate a small portion of the ammoniacal filtrate from 3 nearly to dryness, add a little acetic acid and potassium ferrocyanide. *Red precipitate* or *coloration*, Copper.

5. Precipitate remainder of filtrate from 3 by ammonium sulphide, boil resulting sulphides with dilute H_2SO_4, filter, wash. Residue 7, Filtrate 6.

6. Add ammonia (and if necessary $(NH_4)_2S$). *Yellow precipitate*, Cadmium.

7. Test a portion with borax bead for Ni, Co.

8. Dissolve remainder of precipitate in strong HCl, drive off excess acid, add potassium nitrite and acetic acid, allow to stand 12–24 hours in warm place. *Yellow precipitate*, Cobalt.

9. Add soda in excess. *Light green precipitate*, Nickel. [See note 6.]

IV[4]. (As, Sb, Sn, Au, Pt) (Ni)

A. Add hydrochloric acid to the filtrate from III *A* in slight excess, filter, treat Filtrate VI. Treat filtrate from III *B* in the same manner and collect precipitate on the same filter (but the last

[1] A *dilute* solution. [2] Lead sulphate may also be present, and possibly Au, Pt, Sn.

filtrate is not saved), wash, dry, fuse with sodium carbonate and nitrate, treat with cold water, filter, wash with weak alcohol. Residue 1, Filtrate 5.

1. Heat with hydrochloric acid, add water, a piece of platinum and a fragment of C. P. zinc. When action ceases remove zinc, pour off liquid, warm residue with hydrochloric acid, test the solution with mercuric chloride. *White precipitate*, Tin.

2. Free residue from 1 from Sn by boiling with HCl and washing, warm in a dish, together with the piece of platinum employed in 1, with tartaric acid and water, and a few drops nitric acid added at the last, decant acid solution, test with ammonia and ammonium sulphide. *Orange precipitate*, Antimony.

3. Wash residue from 2, dissolve in aqua regia, evaporate, add ammonium chloride and weak alcohol. *Yellow precipitate*, Platinum.

4. Drive off alcohol from filtrate from 3, add solution ferrous sulphate. *Brown precipitate*, Gold.

5. Acidify with nitric acid, drive off CO_2, add ammonia and magnesia mixture. *White Crystalline precipitate*, Arsenic.

V. (Fe, Al, Cr, Zn, Mn [Ce, Ti])

Boil Filtrate III *C*, filter off S, add a few drops nitric acid, boil. Test a portion after cooling for Iron. If P is suspected and there is not enough Fe to combine, add Fe_2Cl_6 until a drop of the fluid gives a yellowish precipitate on a watch-glass with ammonia. In many cases, more especially in the absence of P, and where traces are not regarded, we can use the scheme *A'*.

A. Drive off excess of acid, add sodium carbonate until the fluid takes the deepest color it will assume without a precipitate, then milk of barium carbonate in slight excess, stir and allow to stand in the cold until the supernatant liquid is colorless; filter, wash. Precipitate 1, Filtrate 3.

A'. Add ammonia in *slight* excess (taking care that the fluid has enough ammonium chloride), heat to near boiling for some time, filter, wash. Precipitate 1, Filtrate 4.

1. Boil with soda, filter, add $(NH_4)Cl$, heat. *Precipitate*, Aluminum.

2. Fuse insoluble residue from 1 with Na_2CO_3 and $NaNO_3$, test for Chromium.

3. Acidify with HCl, boil, precipitate Ba by H_2SO_4. Proceed with filtrate 4.

4. Add ammonia and ammonium sulphide, filter, wash with water containing a little $(NH_4)_2S$. Examine filtrate for Ca and Mg; treat precipitate with acetic acid. Residue 5, Filtrate 7.

5. Treat with dilute HCl. Examine residue for Ni, Co. Filtrate 6.

6. Add nitric acid, concentrate, add soda, boil (if residue, test for Ni, Co if not yet found), filter, test filtrate with ammonium sulphide for Zinc.

7. Boil with soda, test precipitate with Na_2CO_3 for Manganese. [Dissolve a portion of the precipitate in *A* or *A'* in nitric acid, drive off excess NHO_3 and test with molybdic solution for phosphorus. If silica be present, remove before testing for phosphorus by evaporation to dryness.]

VI. (Ba, Sr, Ca, Mg [Li])

If Ba, Sr, Ca, have not been found, the filtrate IV *A* is now examined for small quantities of these bases by ammonium sulphate and oxalate in the usual manner; strontium and calcium sulphates can often be used to advantage in distinguishing Ba and Sr. Test a portion of the filtrate *completely* freed from Ba, Sr, Ca (by ammonium sulphate and oxalate and carbonate if necessary), with sodium phosphate for magnesia, treat remainder as in VII.

VII. (K, Na [Li])

Get rid of all other bases in the usual manner (Baryta water, or milk of lime, ammonium carbonate, ignition). Test for alkalies; with platinic chloride and alcohol for potassium; in filtrate, sodium as platinchloride (and with flame reaction).

NOTES.

It is hardly necessary to advise the testing for each section in a *small* portion of the liquid before proceeding with the main bulk of the solution.

II.

If a precipitate is not formed in the course of a few minutes, the analysis can be proceeded with. The course here laid down is often convenient, but the filtrate from NH_4OH and $(NH_4)_2S$ can be examined in the usual way with ammonium carbonate.

2.

2. Test a portion of the residue in 1 with $(NH_4)_2S$ on a watch-glass, and if Pb is not present, omit 2.

3.

3. Ignite if large quantities of ammonia salts are present.

III.

B. If Cu goes into the filtrate it may interfere to some extent with the detection of Sb. But with care Cu need not be confounded with Sb. If mercuric salts are present, sodium sulphide may give trouble by dissolving mercuric sulphide.

D. HCl and chlorides should be thoroughly washed out in the presence of mercuric salts.

5.

2. Be careful not to precipitate Bi by too great a dilution.

6.

9. In the presence of Cu, test for Ni with the S.Ph bead. If Cu be present, and no Ni, the bead will be green while hot and *blue* when cold. If Ni be present with Cu, the bead will be *green* when cold. If the analyst is not familiar with this test, several S.Ph beads containing varying amounts of Cu and no Ni should be made for comparison. The electrolytic separation may also be used.

IV.

The operator must not depend on the slight excess of $(NH_4)_2S$ dissolving the soluble sulphides, but should treat the first precipitate with a large excess, as indicated in the scheme.

The chemist is supposed to determine the degree of oxidation (or quantivalence) of the elements in the usual way.

VALUATION OF ACETATE OF LIME.

By A. A. Blair.

The wide variation in the results obtained by different methods for the valuation of acetate of calcium (pyrolignite of lime) led me to make the following investigations, which I hope may prove of interest. The distillation method with phosphoric acid is generally

considered the most accurate, but being very troublesome and tedious, is rarely used in commercial work. The carbonate of soda method is much more rapid, but is open to the objection that the solution of crude acetate of lime is so dark in color that it is extremely difficult to mark correctly the end reaction in the titration. Results obtained by calculating the amount of acetate from the lime determined by direct ignition are decidedly untrustworthy, owing to the fact that there is always an excess of base, and the results, consequently, are too high. It occurred to me that, if the solution of crude acetate could be readily decolorised, without changing the composition of the salt, the carbonate of soda method might be made extremely accurate. I therefore made the following experiments: I took a glass tube 50 cm. long and 17 mm. in diameter and closed the lower end with a rubber stopper, through which ran a small glass tube 76 mm. long and 5 mm. in diameter. On top of this stopper I placed a plug of fibrous asbestos 6 mm. thick, and then filled the tube three-quarters full of animal charcoal. Having secured this in a clamp, I filtered through it 5 grams of crude acetate of lime dissolved in 50 cc. of water, and washed it carefully. The solution came through perfectly colorless when the filtration was not too rapid. The rate of filtration is determined by the thickness of the asbestos plug, which can be easily regulated. When properly arranged, the filtration and washing require about two hours. A sample of good grey acetate distilled directly from phosphoric acid yielded as follows:

5 grams acetate, 50 cc. H_2O, 75 cc. H_3PO_4 distilled nearly dry; 50 cc. H_2O added and distilled again; 50 cc. added and distilled a third time. Distillate titrated with NaHO, using phenolphthalein as indicator, gave $Ca(C_2H_3O_2)_2$, 81.72 per cent.

A second determination made in the same way gave $Ca(C_2H_3O_2)_2$, 81.48 per cent.

Two determinations made by the carbonate of soda method, after filtering through animal charcoal, gave: 1st determination, $Ca(C_2H_3O_2)_2$, 81.89 per cent. 2d. determination, $Ca(C_2H_3O_2)_2$, 82.05 per cent.

Direct ignition and calculation from the amount of lime thus obtained gave $Ca(C_2H_3O_2)_2$, 86.02 per cent.

The residue, insoluble in water, was ignited and subtracted from the lime before calculating the latter to $Ca(C_2H_3O_2)_2$.

A second darker sample was taken and gave the following results:

Distilled direct.	Filtered through animal charcoal and distilled.	Na_2CO_3 method filtered through animal charcoal.	Direct ignition.
69.12 per cent.	69.29 per cent.	71.71 per cent.	73.05 per cent.
69.45	69.45	72.04	73.16

I then prepared some acetate of lime from C. P. acetic acid and pure $CaCO_3$, dried it carefully at 105° C. and obtained the following results:

Distilled direct.	Filtered through animal charcoal and distilled.	Na_2CO_3 method direct.
93.18 per cent.	93.49 per cent.	94.93 per cent.

Na_2CO_3 method filtered through animal charcoal.	Ignition.
95.01 per cent.	96.07 per cent.

Combustion of the acetate in chromate of lead and bichromate of potash gave, calculating the CO_2 obtained to $Ca(C_2H_3O_2)_2$, the H in the amount so calculated to H_2O, and the excess of H_2O, found by combustion over the calculated amount, as H_2O in the acetate:

$Ca(C_2H_3O_2)_2$.	H_2O.
92.50 per cent.	5.72 per cent.
92.50	5.83

Using the lime found by ignition, the acetic acid and water as determined by combustion, the composition of the acetate was—

Ca	24.32 per cent.
$(C_2H_3O_2)_2$	69.08
H_2O	5.83
	99.23

A sample of acetate of lime, prepared by filtering the crude pyrolignite through animal charcoal, acidulating with pure acetic acid, evaporating to dryness and drying at 105° C., gave me of $Ca(C_2H_3O_2)_2$—

Direct distillation.	Na_2CO_3 method.	Ignition.	Combustion.
90.01 per cent.	93.92 per cent.	94.49 per cent.	93.68 per cent.
90.25	93.87	...	...
90.25	93.87	...	...
...	93.87	...	...

The composition of the acetate, using the acetic acid obtained by combustion, the lime by ignition and the water by combustion, was—

Ca	23.92 per cent.
$(C_2H_3O_2)_2$	69.97
H_2O	6.55
	100.44

All the samples, both of the crude and pure acetate, were alkaline to litmus, and both the pure samples contained, after long drying at 105° C., considerable water, besides an excess of lime over the amount necessary to form acetate of lime, although the first sample was alkaline at the start, and the second strongly acid with acetic acid.

The samples were all free from magnesia, phosphoric acid, hydrochloric acid, nitric acid and sulphuric acid.

It will be seen, by the comparative results obtained, that the composition of pyrolignite of lime is unaltered by filtering through animal charcoal, while the salt so filtered can be accurately valued by the carbonate of soda method.

The method of procedure I used is as follows:

Treat 5 grams of the pyrolignite with about 50 cc. water and filter through the tube containing animal charcoal as described above. The filtrate and washings should amount to about 250 cc. Heat to boiling in a beaker of about 500 cc. capacity, and add a weighed amount of Na_2CO_3 sufficient to precipitate all the lime as carbonate. Boil with constant stirring until the precipitate, at first floculent, becomes granular, then filter into a flask of about 1 L. capacity and wash thoroughly; add a measured excess of standardised sulphuric acid and boil for a few minutes to expel all CO_2. Cool, transfer to a white porcelain dish of about 1200 cc. capacity, add a few drops of phenolphthalein solution, and titrate with standard NaHO solution.

The method requires: 1. A standard solution of sulphuric acid. 2. A standard solution of caustic soda (to simplify calculation equal in strength to the sulphuric acid solution). 3. Dried Na_2CO_3 of known strength. 4. A solution of phenolphthalein. With the methods for preparing the solutions I give an actual example.

About 30 cc. concentrated C. P. H_2SO_4 to 1 L. water gave, as a means of several determinations by precipitating 20 cc. of the solution with an excess $BaCl_2$ solution,

1 cc. H_2SO_4 sol. = .0508926 gram H_2SO_4 log = 8.7066546
" " = .0550470 gram Na_2CO_3 log = 8.7407344.

NaHO *Solution.*

About 45 grams solid NaHO free from carbonate to 1 L. water gave a solution a little stronger than the H_2SO_4 sol., 20 cc. of the H_2SO_4 solution, diluted to about 1 L. and titrated in the dish after the addition of a few drops of the indicator, required 18 cc. of NaHO sol., then 18 : 20 = 1000 : 1111 ; and by adding 111 cc. of water to the NaHO solution, the latter was reduced to exactly the strength of the H_2SO_4 sol., so that 1 cc. H_2SO_4 sol. = 1 cc. NaHO sol., as was found by a second titration.

Dried Na_2CO_3.

To determine the value of an impure carbonate of soda find value in H_2SO_4 sol., and consequent value in H_2SO_4 ; then $H_2SO_4 : Na_2CO_3$ = value of imp. Na_2CO_3 in H_2SO_4 : value of imp. Na_2CO_3 in pure Na_2CO_3. Then multiply this factor by factor for reducing Na_2CO_3 to $Ca(C_2H_3O_2)_2$, and we have factor for reducing impure Na_2CO_3 to $Ca(C_2H_3O_2)_2$,

$$Na_2CO_3 : Ca(C_2H_3O_2)_2 = 1 : 1.4906 \log = 0.1733512.$$

1 gram impure Na_2CO_3 (the sample I used contained a great deal of water), treated in a flask with 20 cc. H_2SO_4 sol. and boiled to expel CO_2, upon titration with NaHO sol. required 7.25 cc. NaHO sol. to neutralise it, then 20 — 7.25 = 12.75 cc., and second experiment gave 7.35 cc.; 20 — 7.35 = 12.65 cc.

The mean of 2 dets. = 12.70 cc.

1 gram Na_2CO_3 = 12.70 cc. H_2SO_4 sol. Then

log value H_2SO_4 sol.	= 8.7066546
" 12.7	= 1.1038037
" value imp. Na_2CO_3 in H_2SO_4 sol.	= 9.8104583
" ratio $Na_2CO_3 : H_2SO_4$	= 0.0340798
" value imp. Na_2CO_3 in pure Na_2CO_3	= 9.8445381
" " pure Na_2CO_3 in $Ca(C_2H_3O_2)_2$	= 0.1733512
" " imp. Na_2CO_3 in $Ca(C_2H_3O_2)_2$	= 0.0178893

Na_2CO_3 = 106 log = 2.0253059
H_2SO_4 = 98 " = 1.9912261

log ratio = 0.0340798

Value of 1 cc. H_2SO_4 sol. in impure Na_2CO_3. 1 gram = 12.7 cc., or 1 cc. = $\frac{1}{12.7}$, or 1 cc. H_2SO_4 sol. = 0.078741 gram imp. Na_2CO_3 log = 8.8962009.

Solution of Phenolphthalein.

Dissolve in alcohol and deliver the same number of drops from a small pipette for each titration. One drop of NaHO sol. suffices to change the yellow color of the acid solution to a bright and permanent pink.

Example of Valuation of Pyrolignite.

5 grams pyrolignite filtered, and sol. precipitated by 4 grams impure Na_2CO_3, 20 cc. H_2SO_4 sol. added, and when titrated with NaHO sol. it required 19.1 cc. to give the end reaction. Then 20 — 19.1 = 0.9 cc. H_2SO_4, or the excess of impure Na_2CO_3, over and above the amount necessary to precipitate all the lime as carbonate, was equal to 0.9 cc. H_2SO_4 sol.

0.9	log =	9.9542425
Value 1 cc. H_2SO_4 sol. in imp. Na_2CO_3	" =	8.8962009
		18.8504434

or the solution contained 0.07086 gram imp. Na_2CO_3, more than sufficient to precipitate the lime as carbonate. Subtracting this from the 4 grams added we leave 3.92914 grams imp. Na_2CO_3 as the amount necessary to neutralise the acetic acid in the pyrolignite. Then

3.92914	log =	0.5942931
Value of imp. Na_2CO_3 in $Ca(C_2H_3O_2)_2$	" =	0.0178893
4.0943 grams $Ca(C_2H_3O_2)_2$	" =	0.6121824

and dividing this by 5 we leave 0.8189 or 81.89 per cent. $Ca(C_2H_3O_2)_2$ in the pyrolignite.

NOTES ON THE ABSORPTION SPECTRUM OF NITROGEN PEROXIDE.

By L. Bell.

As a preliminary to a more important investigation, I recently had occasion to make a quantitative examination of the absorption bands of nitrogen tetroxide, and obtained results which are of some interest, both as concerning the general laws of gaseous absorption and the special properties of the gas. The definite object in view was the determination of the amount of light actually absorbed in passing through a given column of the gas in question under standard conditions. For this measurement special apparatus had to be devised, since the method used by Vierordt in his similar investigation of the absorption of liquids offers serious mechanical difficulties. Recourse was therefore taken to polarisation, and the apparatus was arranged in the following manner: An ordinary laboratory spectroscope, fitted with a prism for comparison, was used for the observations. Directly in front of the slit was a tin tank with glass ends which contained the absorption tube for the gas. This tank was filled with water so that the gas could be studied at various temperatures. Facing the comparison prism was a pair of Nicol's prisms furnished with a divided circle and a mirror, by which light from the same gas-jet that illuminated the absorption tube could be thrown through the Nicol's prisms upon the comparison prism, and thus on the upper half of the slit. The absorption tube was 10 cm. long in all the experiments. The usual eye-piece was replaced by one having an adjustable slit at its focus. The method of using the apparatus was as follows:

The Nicol's prisms were placed parallel, and the tank of water with the empty absorption tube was placed in position. The light was then arranged, by means of shifting its place and adjusting the mirror, so that it was of the same intensity throughout the field, whether coming directly through the slit or through the Nicol's prisms. The light through the tank formed the upper, and that through the Nicol's prisms the lower half of the field. Then the nitrogen peroxide was admitted to the absorption tube, and one of the absorption bands accurately covered by the slit in the eye-piece. The analyser was then rotated till the upper and lower parts of the field were again of the same intensity, and the angle read off the divided circle. The absorption coefficient was then computed directly

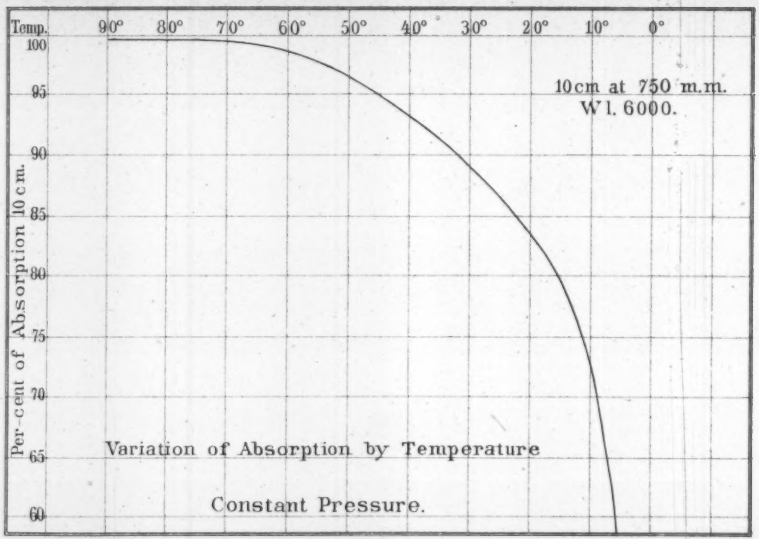
Temp.
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
100
95
90
85
80
75
70
65
60
Per-cent of Absorption 10 cm.
10cm at 750 m.m.
Wl. 6000.
Variation of Absorption by Temperature
Constant Pressure.

FIG. 2.

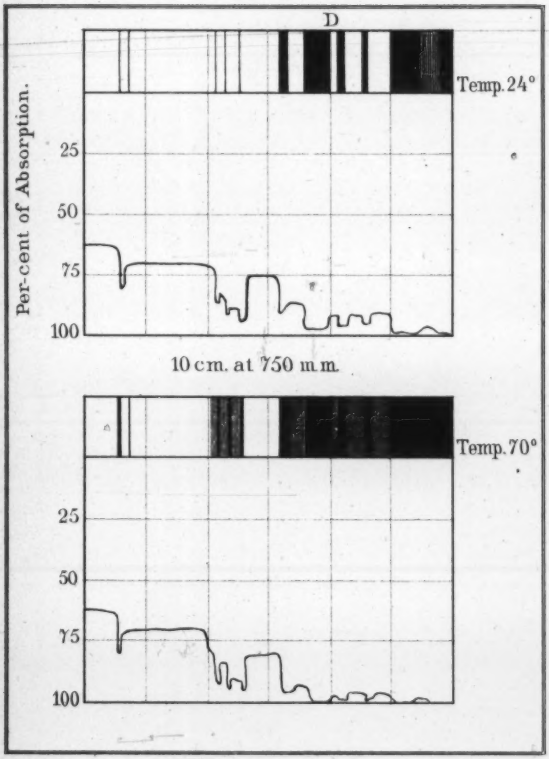
D
Temp. 24°
Per-cent of Absorption.
25
50
75
100
10 cm. at 750 m.m.
Temp. 70°
25
50
75
100

FIG. 1.

from the law of Malus, $I = \frac{\varepsilon}{2} \sin^2 a$. For since a was reckoned from the parallel position of the Nicol's prisms, and $\frac{\varepsilon}{2}$ becomes unity, $k = \sin^2 a$.

The general laws of absorption can be easily tested by this apparatus, but in the experiments only nitrogen peroxide was studied. The gas was made by heating lead nitrate, and was consequently diluted with oxygen, which, however, was advantageous in these preliminary investigations, as it kept the nitrogen peroxide from condensing readily and allowed the use of low temperatures. k was thus determined approximately for every five degrees from 0° to 100°. Small errors were produced by some uncompensated elliptical polarisation in the comparison prism and by possible impurities in the gas. k was obtained as above for all the bands allowing examination through such a range of temperature, and in the case of one, that at *w. l.* 6000, the readings were numerous enough to permit the construction of a tolerably accurate curve. All the observations were made at constant pressure.

Fig. 1 shows the change in the spectrum produced by change of temperature, the curve giving the amounts of light absorbed.

Fig. 2 shows the progressive changes in the band at *w. l.* 6000.

At 0° the gas was of a very pale orange color, and gradually darkened with heating till at 100° it was dark red. As is well known, this change of color is accompanied by a gradual change from the molecular form N_2O_4 to NO_2. The changes produced in the absorption spectrum by this change of composition are by no means well known. Lockyer[1] states that there is a marked change from the spectrum of the one molecular form into that of the other, while Roscoe and Schorlemmer[2] state that the change in color cannot be recognised by any equally striking change in the spectrum. It is the object of these notes to throw, if possible, a little light on this matter. Let us look at the data already known.

First. The liquefied gas forms colorless crystals at 9°, and while the liquid just above this temperature is colorless, it gradually changes color up to its boiling point.

Second. Deville and Troost[3] have shown that while the gas at 140° consists almost entirely of NO_2, it is not completely reduced to N_2O_4 at its boiling point, 22°.

[1] Nature **10**, 89. [2] Treatise on Chemistry **1**, 427. [3] Comp. Rend. **64**, 257.

Third. The vapor density of the gas, as determined by Playfair and Wanklyn,[1] shows that even at 0° it consists in part of NO_2.

Fourth. M. Gernez[2] has shown that the absorption spectrum of the liquid gas consists of the principal bands of the gaseous spectrum.

In my own experiments it appeared,

First. That while there is a very striking increase of both general and selective absorption produced by heating, none of the bands disappear at a high temperature. Some of the gas was even sealed up in a glass tube and heated in the flame of a Bunsen burner till the glass softened, but the bands were still permanent. As the tube was rather small in diameter, the actual appearance of the spectrum at this temperature was singularly like that of a longer column at 0°.

Second. The determinations of k show that none of the bands increase in darkness when the temperature falls; k for each band increasing with the temperature.

Third. The rate of variation of k points to the complete disappearance of absorption at a temperature not far below 0°.

Now what inference can we draw from these facts? Evidently this: It is highly probable that nitrogen peroxide in the molecular form N_2O_4 produces no absorption spectrum at all.

If it had a spectrum the absorption would certainly increase with the amount present, *i. e.* the length of column. But no such increase takes place, and the well-known bands remain at a temperature where it is certain that N_2O_4 is absent. Hence we may conclude that the absorption spectrum of nitrogen peroxide is entirely due to the molecular form NO_2, and that in the form N_2O_4 (as in the crystals) the compound is colorless.

In this case it is clear that the effect of the presence of N_2O_4 is simply dilution. Therefore the amount of NO_2 in the compound at any given temperature is measured by the absorption at that temperature. Hence the percentage of NO_2 can be estimated from the measured absorption at a temperature where the composition is known, as at 100° from Deville's experiments. Probably the best method would be graphical interpolation from measurements of the absorption of columns of 1, 2, 3 . . . cm. of gas. I shall hope eventually to apply the above method in connection with an accurate determination of the various values of k.

[1] Chem. Soc. J. **15**, 156. [2] Comp. Rend. **74**, 465.

SPECTROSCOPIC DETERMINATION OF LITHIUM.

By L. Bell.

Various attempts at quantitative spectroscopy have from time to time been made, but in general they have not met with success.

Recently, however, I have found that such a method may be applied to certain estimations with sufficient ease and accuracy to warrant calling attention to it. Lithium, notoriously difficult to determine by the usual methods, gives such a delicate spectral reaction that it proved a particularly good subject for investigation.

The method used was as follows: A standard solution was made from lithium carbonate converted to the chloride, containing .0265 milligram of Li_2O per cc. 10 cc. of this were taken, diluted till the spectral line was just on the point of vanishing, and the volume noted. Then the solution to be estimated was diluted to the same point and its volume compared with that of the standard, when a simple proportion gave the amount of Li_2O present in it.

Several variations in the method were tried, but the best results were reached when the following precautions were taken: The solutions should be tested with a *very small* loop in the platinum wire, which should not be changed, but burned clean after each trial. The Bunsen burner should not be regulated during the experiment, and the wire should always be applied to the same part of the flame. Dilution should be continued till the line is in each case barely, though constantly, visible.

A series of determinations was made to test the accuracy of the method, the amount of lithium present being in no case previously known, and the last three being solutions made up by another person.

	Determined.	Actually present.
(1)	1.5 mg.	1.4 mg.
(2)	0.7	0.7
(3)	0.9	0.7
(4)	1.1	0.9
(5)	0.9	0.8
(6)	0.6	0.5
(7)	0.7	0.7
(8)	0.29	0.32
(9)	0.42	0.40
(10)	0.68	0.55

Parallel determinations were made of the lithium in a specimen of muscovite which gradually merged into lepidolite.

	Amount analysed.	Per cent. of Li_2O.
Analysis I,	92.8 mg.	00.88
Analysis II,	90.9	00.73
Average,		00.8

Also a single estimation of the Li in the Rozena lepidolite:

Amount analysed = 81.1 mg. Per cent. Li_2O = 5.3. The recorded analyses vary from 1.27 to 5.88 per cent.

The advantages of this means of determination seem to be, first, it can be used with considerable accuracy in cases where the per cent. of lithium is very small, even so small as to defy even approximation by any other method; second, it can be readily used when the amount of the substance available is too small for ordinary analysis; third, it is simple and rapid, as it is only necessary to get the substance into solution, and for small amounts of lithium, at least as accurate as the usual process.

The method can be used for such other elements as give distinct and persistent spectral lines, particularly thallium. Ca, Sr, Ba, K, do not give lines sufficiently persistent except in rather strong solutions, and the same is true of Rb and Cs, while Na is so ubiquitous as to give very uncertain results.

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Contributions from the Sheffield Laboratory of Yale College.

XXII.—INFLUENCE OF BILE, BILE SALTS AND BILE ACIDS ON AMYLOLYTIC AND PROTEOLYTIC ACTION.

By R. H. Chittenden and Geo. W. Cummins.

The influence of bile and bile acids on the digestive processes of the intestinal canal has long been considered an important one, still few experiments have been made to determine the exact influence of these substances by themselves on ferment action. The form in which the main constituents of the bile exist in the intestinal canal depends naturally upon the reaction of the contents

of the intestines. If these have an acid reaction, bile acids must be present; if alkaline, salts of these acids; and it is fair to presume that under these two conditions the presence of bile may be productive of different effects on ferment action. Recorded observations tend to show that ordinarily the contents of the intestines possess a distinct acid reaction; thus Schmidt-Mülheim[1] has found that in dogs fed on albuminous matter the contents of the small intestines are invariably acid, although the mucous membrane sometimes possesses an alkaline reaction. It is evident that in such cases the alkali of the bile must have combined with the acid of the chyme, which would be followed by liberation of the bile acids and partial precipitation of the same in combination with the proteid matters of the chyme. Moreover, the recorded observations of Schmidt-Mülheim tend to show that this acid condition of the contents of the intestines persists throughout the entire length of the intestinal canal. Uffelmann[2] has likewise found, in corroboration of the above, that the faeces of infants naturally nourished possess a weak acid reaction, while, on the other hand, Nothnagel,[3] as a result of 800 observations, finds that human excrement, in the case of adults, varies decidedly in its reaction, being generally alkaline, more rarely acid or neutral. It is hardly proper, therefore, to conclude that it is only necessary to study the influence of the bile acids in their free condition on ferment action, since in the passage of the ferments through the intestinal canal there are times, doubtless, when the reaction of the mass is more or less alkaline, especially in the small intestines, for some distance beyond the opening of the bile and pancreatic ducts. In either case it is an interesting point to ascertain whether the bile salts have an action at all analogous in kind or extent to that of the free acids.

Many observations[4] are recorded concerning the duodenal precipitate formed in the duodenum by the action of bile on the acid-reacting chyme. The precipitate itself has generally been supposed to consist of a mixture of syntonin, peptone and bile acids, but recent experiments of Maly and Emich[5] with pure bile acids tend to show that only the non-peptonised albuminous bodies are precipitated, viz. coagulable albumin and syntonin, and

[1] Archiv. für Physiologie. Du Bois Reymond, 1879, p. 56.
[2] Jahresbericht für Thierchemie, 1881, p. 305.
[3] Jahresbericht für Thierchemie, 1881, p. 309.
[4] See Maly in Hermann's Handbuch der Physiologie **5**, 180.
[5] Monatshefte für Chemie **4**, 89.

these only by taurocholic acid, while peptone and "propeptone" remain in solution. This fact lends favor to the view advanced by Hammarsten, that the object of the precipitation of the albuminous matter on the walls of the intestines is to prevent its too rapid passage through the intestinal canal, thus escaping the full action of the pancreatic juice. The addition of taurocholic acid to a solution of peptone, Maly and Emich find, is followed by the formation of a distinct opalescence or fine dust-like precipitate, slowly changing to fine droplets. This precipitate, however, which is doubtless the same as observed by Hammarsten and Brücke on the addition of bile to portions of a digestive mixture, does not contain, according to Maly and Emich, any peptone, but consists of taurocholic acid, possibly in a modified form.

Both of these precipitations, however, would tend to mechanically throw down, to a greater or less extent, any ferment present, and thus diminish ferment action; but, as Maly points out, the main reason for a diminished action, in the case of pepsin, is to be sought for, not in a precipitation of the ferment, but in the formation of a compound of albumin with the bile acid, not digestible by pepsin-hydrochloric acid. But since this precipitation, as a normal reaction in the animal body, must take place in the intestinal canal, it is equally important to ascertain the extent of its digestibility in pancreatic juice, or, in other words, to ascertain the exact influence of bile and its several constituents on the proteolytic action of trypsin as well as on the action of pepsin and on amylolytic action.

The only data bearing on these points are the recent experiments of Maly and Emich, who have found that 0.2 per cent. taurocholic acid hinders the digestive action of pepsin-hydrochloric acid, while 1 per cent. glycocholic acid is without influence. The same investigators likewise state that 0.1 per cent. taurocholic or glycocholic acid stops the amylolytic action of the pancreas ferment, and that 0.2 per cent. taurocholic acid or 1 per cent. glycocholic acid will completely stop the amylolytic action of the salivary ferment.

Our experiments on this subject were commenced before the above results were published, and we have continued them, since we wished to ascertain also the influence of the bile salts, and also the effects of both salts and acids, as well as the bile itself, on the proteolytic ferment of the pancreas. The results of Maly and Emich, moreover, not being quantitative, do not express the relative effects of the various percentages of bile acids used, but simply the

percentage of acid necessary to stop the ferment action under the conditions described by them.

1.—*Influence on Amylolytic Action.*

As amylolytic ferment, we have employed filtered human mixed saliva, made neutral and then diluted to a known volume. In studying the influence of the various percentages of bile salts and acids on the action of the ferment we have used a digestive mixture (50 or 100 cc.) containing 1 per cent. of starch previously boiled with water, and 2 per cent. of saliva, together with the given percentages of bile salts or acids. The extent of diastatic or amylolytic action under the varying conditions was determined in each case by estimating the amount of reducing substances, maltose and dextrose, formed during 30 minutes warming at 40° C. Further diastatic action was at once stopped by boiling the digestive mixtures, after which they were diluted to a known volume, and the reducing substances determined in a given portion of the diluted fluid by Allihn's gravimetric method.[1] The reducing substances are in each instance calculated as dextrose, and the diastatic action is expressed in the percentage of starch converted into sugar.

We first tried the influence of crystallised ox bile, since bile itself contains a small amount of a diastatic ferment. A 1 per cent. solution of nicely crystallised ox bile was made, with which the following results were obtained:

Crystallised bile.	Weight Cu in one-eighth.[2]	Total amount sugar.	Starch converted.
0 per cent.	0.0643 gram.	0.2636 gram.	23.72 per cent.
0.01	0.0630	0.2584	23.25
0.02	0.0686	0.2804	25.23
0.03	0.0693	0.2836	25.52
0.05	0.0656	0.2688	24.19
0.10	0.0734	0.3000	27.00
0.20	0.0665	0.2724	24.51
0.35	0.0447	0.1860	16.74

Here it is plain that a mixture of sodium glycocholate and taurocholate, in such proportion as they are contained in crystallised ox bile, exerts no appreciable retarding influence on amylolytic

[1] Zeitschrift für analytische Chemie **22**, 448.
[2] One-eighth of the entire digestive mixture.

action until present to the extent of 0.35 per cent. On the contrary, smaller percentages unmistakably tend to increase the diastatic action of the ferment. The solution of crystallised bile had, however, a slight acid reaction, and possibly this may have had some influence in giving the latter results. The saliva and starch were both neutral.

Experiments were next tried with sodium taurocholate alone, and also with sodium glycocholate. Following are the results:

Sodium taurocholate.	Weight Cu in one-eighth.	Total amount sugar.	Starch converted.
0 per cent.	0.0787 gram.	0.3212 gram.	28.90 per cent.
0.3	0.0030	0.0146	1.51
0.5	0.0023	0.0112	1.00
Sodium glycocholate.			
0.5 per cent.	0.0783	0.3196	28.76

It is thus plainly evident that sodium taurocholate has a very decided action on the amylolytic ferment of saliva, while the same percentage of glycocholate is entirely without effect. The retarding action of the crystallised bile is thus, without a doubt, due wholly to the taurocholate. Moreover, even smaller percentages of sodium taurocholate retard amylolytic action with almost equal energy.

The following results were obtained under like conditions as the preceding, except that the 2 per cent. of saliva employed was not neutralised:

Sodium taurocholate.	Weight Cu in one-fourth.	Total amount sugar.	Starch converted.
0 per cent.	0.0590 gram.	0.1212 gram.	21.81 per cent.
0.14	0.0079	0.0192	3.45
Sodium glycocholate.			
0.20 per cent.	0.0758	0.1548	27.86

Thus even 0.14 per cent. of sodium taurocholate under these conditions almost entirely stops amylolytic action. The smaller percentage of glycocholate, however, causes the same increased amylolytic action observed with the smaller percentages of crystallised bile.

With the bile acids the following results were obtained. The glycocholic acid used was a nicely crystallised specimen prepared

from ox bile, while the taurocholic acid, prepared from the same source, was amorphous:

Per cent. bile acid.	Weight Cu in one-fourth.	Total amount sugar.	Starch converted.
0	0.0694 gram.	0.1420 gram.	25.56 per cent.
0.01 taurocholic	0.0753	0.1538	27.68
0.05	0.0783	0.1598	28.76
0.10	0.0060	0.0146	2.63
0.20	0		
0.05 glycocholic	0.0523	0.1082	19.47
0.10	0.0095	0.0234	4.21
0.20	0.0056	0.0136	2.44
0.50	trace		
1.00	0		

It is thus seen that 0.1 per cent. taurocholic acid prevents amylolytic action almost entirely, while 0.2 per cent. does not allow the conversion of any starch into sugar. This agrees exactly with the results obtained by Maly and Emich.[1] These same investigators, however, found only a trace of amylolytic action in the presence of 0.05 per cent. taurocholic acid, a result which does not agree with what we have found, working, however, under somewhat different conditions.

The presence of 1.0 per cent. glycocholic acid entirely prevents the conversion of starch into sugar, while 0.5 per cent. allows only the smallest amount of diastatic activity. Maly and Emich likewise found that 1.0 per cent. glycocholic acid stopped the diastatic action of saliva.

We have repeated the last series of experiments in part, using, however, normally alkaline saliva instead of neutralised.

Per cent. bile acid.	Weight Cu in one-fourth.	Total amount sugar.	Starch converted.
0	0.0590 gram.	0.1212 gram.	21.81 per cent.
0.1 glycocholic	0.0107	0.0258	4.64
0.2	0.0057	0.0139	2.50
0.1 taurocholic	0.0052	0.0126	2.26

These results agree exactly with the preceding, and both together plainly show that only small percentages of bile acids are required to entirely prevent the amylolytic action of saliva.

[1] *Loc. cit.* 118.

Assuming that the amylolytic ferment of the pancreatic juice is similar in its nature to the ferment of saliva, it would follow from our experiments that whether the contents of the intestines are acid or alkaline, the presence, beyond a certain percentage, of taurocholic acid, either as free acid or as a taurocholate, would tend to diminish amylolytic action. Very small percentages, however, would have little, if any, retarding effect, indeed might even increase amylolytic action. As to glycocholic acid, the free acid is much more powerful in its action on the amylolytic ferment than the sodium salt of the acid.

Considering these results in the light of a possible application to changes in the intestinal canal, it becomes an interesting point to ascertain whether bile itself exerts the same influence on amylolytic action as the bile salts. Moriggia and Battistini[1] state that while bile mixed with chyme gives a precipitate which, among other things, contains mucin, bile acids and pepsin, thus hindering gastric digestion, it does not, on being mixed with saliva, hinder its amylolytic action. This they found to be the case both with bile containing mucin and with bile from which the mucin had been removed by acidifying. We have, therefore, made the following experiments with fresh ox bile containing 7.46 per cent. of solid matter. The digestive mixtures contained as before 1 per cent. of starch, 2 per cent. of neutral saliva, and were warmed at 40° C. for 30 minutes:

Ox bile.	Weight Cu in one-eighth.	Total amount sugar.	Starch converted.
0 per cent.	0.0753 gram.	0.3072 gram.	27.64 per cent.
2.0	0.0875	0.3568	32.11
5.0	0.0690	0.2824	25.41
10.0	0.0719	0.2944	26.50
20.0	0.0770	0.3144	28.30

Here, in close accord with what has been found before, the presence of a small percentage of bile causes increased amylolytic action; larger percentages, however, have little, if any, effect; certainly not such an effect as would be expected from the known action of the bile salts. The bile itself possessed to a slight extent, diastatic action; 20 cc. of the bile (20 per cent.) converting 4.53 per cent. starch into sugar in 30 minutes. This,

[1] Jahresbericht für Thierchemie, 1876, p. 196.

however, could hardly account for the increased amylolytic action noticed above in the presence of 2 per cent. of bile. Wittich[1] and also Hofmann have noticed the occasional diastatic action of bile, Wittich even extracting the ferment from human bile by his glycerine method. Gianuzzi and Bufalini[2] have shown that the action varies considerably in bile from different animals and individuals, and without any apparent dependence upon the nature of the food. Ewald[3] states that the diastatic capacity of bile appears to be slight in all cases, and is not found in bile which has stood for some time. We have found, however, in bile from several animals considerable diastatic power; thus in one sample of fresh sheep's bile, 25 cc. (25 per cent.) converted 24.33 per cent. of starch into sugar in 30 minutes at 40° C. We have likewise found great variation in diastatic power, varying, expressed in the percentage of starch converted into sugar under the conditions described, from 4 to 24 in the case of herbivorous animals. We have also noticed in bile from sheep and oxen the presence of a small amount of sugar, or at least a substance capable of reducing Fehling's solution. In one instance the amount was not inconsiderable; 25 grams of ox bile yielding, by Allihn's method, 0.040 gram metallic copper, equal to 0.0209 gram dextrose or 0.08 per cent. Naunyn, we believe, has already claimed the presence of sugar in bile.

While we know then that the bile acids and bile salts by themselves retard very decidedly the amylolytic action of ptyalin, it would appear that the retarding influence of the latter may be, in part at least, counteracted by other substances naturally present in the bile.

2.—*Influence on the Proteolytic Action of Pepsin.*

It has long been known that bile has a retarding action on pepsin digestion, and Maly and Emich have recently shown the percentages of bile acids necessary to bring the action of pepsin to a standstill. We have, however, in addition, experimented with bile itself, and as in the case of the amylolytic ferment, have endeavored to study the influence of the bile acids quantitatively. The method employed for measuring proteolytic action is one frequently used in this laboratory, and which has invariably given satisfactory

[1] Jahresbericht für Thierchemie, 1872, p. 243.
[2] Jahresbericht für Thierchemie, 1876, p. 197.
[3] Lectures on Digestion. Amer. ed. p. 77.

results. The only feature which calls for description is the preparation of the proteid matter to be digested. The material consists of carefully selected and thoroughly washed blood fibrin. All soluble matters are removed by successive extraction with boiling water, cold and boiling alcohol, and finally with cold and warm ether. The fibrin is thus obtained in a perfectly friable condition and can easily be ground to a coarse powder. It is then dried at 100–110° C. This material is well adapted for quantitative experiments with pepsin-hydrochloric acid; the residue remaining after a digestion can be rapidly filtered with the aid of a pump, and can be easily freed, by washing, from peptones and other soluble products of digestion.

The gastric juice employed in the experiments consisted of a hydrochloric acid solution of a glycerine extract of pig's stomach, in the proportion of 10 grams glycerine extract to one litre of 0.2 per cent. hydrochloric acid. 50 or 100 cc. of this pepsin-hydrochloric acid were employed in each experiment, to which was added 1 or 2 grams of the dried fibrin (1 per cent.), together with the given percentage of bile or bile acids.

We first tried the influence of bile itself, using fresh ox bile, slightly alkaline in reaction and containing 10.02 per cent. of solid matter.

The digestive mixtures were warmed at 40° C. for two hours, then filtered at once and the undigested residue washed thoroughly,[1] and then dried at 100° C. until of constant weight. Following are the results of the first series of experiments, with 2 grams of fibrin and 100 cc. of gastric juice:

Bile in digestive mixture.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1957 gram.	90.21 per cent.
0.25	0.1890	90.55
0.50	0.2050	89.75
1.00	0.2234	88.83
3.00	0.5453	72.73
5.00	0.7642	61.84

[1] In all of the pepsin-hydrochloric acid digestions the presence of bile or bile salts naturally causes more or less of a precipitate, dependent in amount upon the percentage of bile and also upon the amount of digestive products. In washing the undigested fibrin it was of course necessary to remove this precipitate. This was accomplished by pouring over the precipitate on the filter 50 cc. of 0.5 per cent. potassium hydroxide and then washing with water until the alkali was wholly removed. The following experiment shows that under these conditions the alkali affects the swollen fibrin but little, if any. Two portions of fibrin of 2 grams each were warmed with 100 cc. of 0.2 per cent. HCl for 30 minutes, then filtered and one washed with water alone, the other with water and alkali. The first gave 1.9272 grams dried residue, the other 1.9155 grams.

A second series, tried under the same conditions, but with larger percentages of bile, gave the following results:

Bile in digestive mixture.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1979 gram.	90.10 per cent.
0.25	0.2456	87.72
0.50	0.1927	90.36
9.00	1.1955	40.22
13.00	1.6611	16.94
16.50	1.7812	10.94
20.00	1.9241	3.29

From these two series of experiments it is evident that the presence of bile, from 1 per cent. upward, causes diminished proteolytic action, the retarding effect being proportionate to the amount of bile present. 20 per cent. of bile stops the action under these conditions almost completely. It is fair to presume, therefore, that the reflux of but a small amount of bile into the stomach would be productive of a diminished proteolytic action.

These results therefore agree with the older statements of Brücke, Hammarsten and others to the effect that bile added to a gastric digestion has the effect of bringing the proteolytic action to a standstill.

We next tried the influence of the individual bile acids with the following results:

Taurocholic acid.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1311 gram.	86.89 per cent.
0.025	0.1461	85.39
0.050	0.2200	78.00
0.100	0.2421	75.79
0.200	0.2668	73.32
0.500	0.3579	64.21

Here it is seen that the smallest percentage of taurocholic acid added produces a distinct effect on proteolytic action, and in the next series of experiments still smaller percentages of acid caused an equally marked effect. In both series of experiments the mixtures were warmed at 40° C. for 1 hour and 30 minutes.

Taurocholic acid.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1499 gram.	85.01 per cent.
0.010	0.1819	81.81
0.015	0.1900	81.00
0.020	0.2947	70.53
0.050	0.3110	68.90

Adding the taurocholic acid to the digestive mixture in the form of a sodium salt has the effect of diminishing still further the action of the ferment; doubtless a larger percentage of the acid remains in solution in this case.

Taurocholic acid.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.2059 gram.	79.41 per cent.
0.1	0.6198	38.02
0.2	0.6426	35.74
0.5	0.6475	35.25

Maly and Emich found that 0.2 per cent. taurocholic acid entirely stopped the action of pepsin; in our experiments, however, ferment action was still manifest even in the presence of 0.5 per cent. acid. Whether this difference in result is due to difference in the acid used, or to difference in method, we cannot say. Glycocholic acid we found to be entirely without influence on the action of pepsin, as did also Maly and Emich.

3.—*The Proteolytic Action of Trypsin in Neutral, Alkaline and Acid Solutions.*

The trypsin solution was prepared according to Kühne's method,[1] from dried pancreas freed from fat; the solution after neutralisation always contained some sodium salicylate, sufficient to prevent putrefaction during short digestive periods. According to Kühne,[2] trypsin acts quite energetically, both in neutral and salicylic acid solutions, but most energetically when the pancreatic solution contains 0.3 per cent. sodium carbonate. According to Heidenhain[3] the action of definite percentages of sodium carbonate varies with the amount of ferment.

We have tried quantitative experiments, as a preliminary to studying the influence of bile, with the following results;[4] the mixtures were warmed at 40° C. for 3 hours and 40 minutes, and contained 2 per cent. of fibrin:

[1] Untersuchungen aus der physiolog. Inst. d. Universität Heidelberg **1**, 222.

[2] *Ibid.* p. 223. [3] Pflüger's Archiv **10**, 576

[4] The pancreatic juice was prepared from 20 grams dry pancreas, and finally diluted to 1000 cc. 50 cc. were used in each digestion with 1 gram of pure fibrin.

Reaction of the fluid.	Weight of undigested residue.	Fibrin digested.
neutral,	0.2312 gram.	76.88 per cent.
0.1 per cent. Na_2CO_3,	0.1570	84.30
0.2	0.0925	90.75
0.3	0.0772	92.28
0.4	0.0426	95 74
0.5	0.1038	89.62
0.1 per cent. salicylic acid,	0.5651	43.49

With a larger percentage of fibrin and a longer period of digestion the results are somewhat different. The following were obtained with 4 per cent. fibrin in 6 hours and 40 minutes at 40° C.:

Reaction of the fluid.	Weight of undigested residue.	Fibrin digested.
neutral,	0.3785 gram.	62.15 per cent.
0.1 per cent. Na_2CO_3,	0.2581	74.19
0.2	0.1395	86.05
0.3	0.1588	84.12
0.4	0.1629	83.71
0.5	0.1318	86.82
0.1 per cent. salicylic acid,	0.4728	52.72

An average of the two series of results plainly shows that there is but little difference in digestive action in the presence of 0.2–0.5 per cent. sodium carbonate, although in a given solution a change in the percentage of alkali is at once manifest, to a slight extent, in the amount of fibrin digested. Greatly increased percentages of alkaline carbonate materially diminish the action of the ferment, as the following series of experiments indicate; the mixtures were warmed for 2 hours at 40° C.:

Reaction of the fluid.	Weight of undigested residue.	Fibrin digested.
neutral,	0.5863 gram.	41.37 per cent.
0.5 per cent. Na_2CO_3,	0.1584	84.16
1.0	0.3760	62.40
2.0	0.7010	29.90
3.0	0.7892	21.08
4.0	0.8373	16.27
5.0	0.8608	13.92

The difference in action between a neutral trypsin solution and a solution containing salicylic acid is quite noticeable, at the same time it is evident that in the acid-reacting fluid the trypsin simply

acts more slowly, and if time be given, the action will approach more closely to that of the neutral solution. It is of course understood that the salicylic acid in the above experiments does not exist in the free state, but in combination with the proteid matter present, and doubtless in most of the experiments recorded, where trypsin has been exposed to the action of small fractions of a per cent. of acid, no free acid has been present, but only varying percentages of acid-proteids.[1] Kühne[2] has pointed out that hydrochloric acid above 0.05 per cent. is injurious to the action of trypsin, and Heidenhain[3] has shown that the addition of 0.1 per cent. hydrochloric acid to an aqueous extract of the pancreas stops its action. C. A. Ewald,[4] however, found that while pepsin-hydrochloric acid destroyed trypsin, trypsin could digest fibrin in the presence of 0.3 per cent. hydrochloric acid. Mays[5] likewise found that trypsin digestion could take place in the presence of 0.3 per cent. hydrochloric acid, but only when a relatively large proportion of fibrin was present, and in corroboration of Kühne's statement, he showed that trypsin could be destroyed both by pepsin and dilute hydrochloric acid. Engesser[6] found that a pancreatic juice did not lose its tryptic power by two hours warming with a gastric juice containing 0.5 per cent. hydrochloric acid. Langley,[7] on the contrary, has shown that a glycerine extract of the pancreas loses a very appreciable amount of trypsin when warmed for two and a half hours with 0.05 per cent. hydrochloric acid. Lindberger,[8] working with an alcohol precipitate from a glycerine extract of ox pancreas, in which there would naturally be present but a small amount of proteid matter in addition to the trypsin, found that in the presence of 0.1 per cent. hydrochloric acid the ferment was entirely without action, and even in the presence of 0.012 per cent. hydrochloric acid, fibrin was much more slowly dissolved than by a neutral trypsin solution. Lindberger, moreover, found that weaker acids, as acetic and lactic, had a much different effect than the stronger hydrochloric acid; thus with dilute acetic acid digestion of the fibrin was almost as rapid as with a neutral solution of trypsin, while with small amounts of lactic acid, the ferment

[1] See Danilewsky. Centralbl. med. Wiss. 1880.
[2] Vehr. Naturhist. med. Vereins zu Heidelberg, 1877, p. 193.
[3] Pflüger's Archiv **10**, 578.
[4] Jahresbericht für Thierchemie, 1880, p. 297.
[5] Untersuch. a. d. physiolog. Inst. d. Univ. Heidelberg **3**, 378, 1880.
[6] Jahresbericht für Thierchemie, 1880, p. 297.
[7] Journal of Physiology, Vol. 3, No. 3.
[8] Jahresbericht für Thierchemie, 1883, p. 281.

action was even more energetic than in a neutral solution. There is, however, no guarantee that in these experiments free acid was present.[1]

We have found that *free* acids, even when present in small percentages, completely stop the proteolytic action of trypsin; and that when considerable albuminous matter is present, the action of trypsin is much hindered by the addition of acid to a neutral solution even before the proteid matters present are saturated with acid. 0.1 per cent. *free* salicylic acid, in the presence of proteids already saturated with the acid, allows no proteolytic action whatever. On the other hand, a sufficient amount of proteid matter just saturated with hydrochloric acid, no free acid being present, will almost completely stop the action of trypsin. Proteid matter, however, only partially saturated with acid has a much smaller retarding action. This, doubtless, was the condition of the mixtures in Mays' and Engesser's experiments above referred to, for, as Mays states, the ferment could act in the presence of 0.3 per cent. hydrochloric acid only when a relatively large proportion of fibrin was present.

A pancreatic juice prepared from 20 grams of dried pancreas by warming it at 40° C. with 200 cc. 0.1 per cent. salicylic acid, etc., was finally made exactly neutral and diluted to 500 cc.; 25 cc. of this solution required 7.5 cc. of a 2.0 per cent. solution of salicylic acid to completely saturate the proteids present,[2] the excess of free acid necessary to give the tropaeolin reaction being deducted.

Three digestive mixtures were made as follows:

1. 25 cc. of the neutral pancreatic solution + 50 cc. water.

2. 25 cc. of the same pancreatic solution + 7.5 cc. 2.0 per cent. salicylic acid solution + 17.5 cc. water. The mixture was acid to test papers, but gave no reaction with tropaeolin. It therefore contained no free acid, but 0.3 per cent. of combined acid.

3. The same as No. 2, but 2.5 cc. more of 2.0 per cent. salicylic acid, so that the solution contained, in addition to the acid proteids, 0.1 per cent. free salicylic acid.

1 gram of fibrin was added to each of these and the mixtures

[1] We have seen only the abstract of Lindberger's paper, so cannot speak positively on this point.

[2] Tested by tropaeolin oo according to the method of Danilewsky (Centralbl. med. Wiss. 1880). One drop of a solution containing 0.028 per cent. free salicylic acid gives a reddish violet color, which is, however, not permanent as in the case of hydrochloric acid, but transient. With hydrochloric acid, one drop of a 0.003 per cent. solution will give the reaction.

warmed at 40° C. for 8 hours and 40 minutes. No. 1 digested 88.34 per cent. of the fibrin; No. 2, 13.44 per cent., while No. 3 had no action whatever.

Much smaller percentages of combined salicylic acid cause an equally diminished proteolytic action; thus, in the case of a carefully dialysed juice where the proteid matter was much diminished, the digestive mixture, with its proteids wholly saturated, contained but 0.060 per cent. of combined salicylic acid; yet this mixture, in 15 hours at 40° C., digested but 17.10 per cent. of fibrin, while the same amount of the neutral trypsin solution digested 57.80 per cent. Combined hydrochloric acid has a greater hindering action than salicylic acid, as the following results show:

Pancreatic solution of trypsin.	Fibrin digested in 18 hours.
neutral,	57.80 per cent.
0.034 per cent. combined HCl + no free HCl	3.90
0.034 " " HCl + 0.005 per ct. HCl	2.31
0.034 " " HCl + 0.010	0.87

It is thus evident that in an ordinary digestive mixture, or even where albuminous matter is present only in limited quantity, the addition of hydrochloric or salicylic acid to a neutral solution of trypsin reduces its proteolytic action to a minimum before any free acid is present.

4.—*Influence of Bile, Bile Salts and Bile Acids on the Proteolytic Action of Trypsin.*

The addition of bile to a *neutral* pancreatic juice causes but little change in its proteolytic action, as is seen from the following results obtained with ox bile containing 8.3 per cent. solid matter:

Bile.	Wt. of undigested fibrin.	Fibrin digested.
0 per cent.	0.4118 gram.	59.82 per cent.
1.0	0.3907	60.93
10.0	0.3938	60.62

A slightly increased action is the only effect produced on the trypsin.[1] The addition of bile to an *alkaline* pancreatic juice does not produce any very different results. The following were obtained with a pancreatic juice containing 0.3 per cent. sodium carbonate and fresh ox bile containing 10.02 per cent. solid matter:

[1] Compare Heidenhain, Pflüger's Archiv **10**, 579.

Bile.	Wt. of undigested residue.	Fibrin digested.
0 per cent.	0.3056 gram.	69.44 per cent.
0.25	0.3074	69.26
0.50	0.3488	65.12
1.00	0.3633	63.67
5.00	0.3278	67.22
10.00	0.3603	63.97

Here there is no increased proteolytic action, neither is there any very great retarding effect produced. Pure sodium glycocholate and taurocholate produce results similar to bile, as the following table shows. The pancreatic juice contained 0.3 per cent. sodium carbonate:

Sodium taurocholate.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.2308 gram.	76.92 per cent.
0.05	0.2566	74.34
0.10	0.3048	69.52
1.00	0.2832	71.68
Sodium glycocholate.		
0.10 per cent.	0.2576	74.24
0.20	0.3154	68.46

The presence of 3.0 per cent. crystallised ox bile caused a somewhat different result, increasing the proteolytic action slightly; thus, while the control, containing 0.3 per cent. sodium carbonate, digested 88.69 per cent. fibrin, the same trypsin solution plus 3 per cent. of crystallised bile digested in the same time 89.73 per cent. fibrin.

While bile or bile salts have but little influence on the proteolytic action of trypsin, the bile acids, even small percentages, have a much more marked effect. The following results, obtained by the addition of the bile acids to a neutral pancreatic juice, show the extent of the action:

Bile acids.	Weight of undigested residue.	Fibrin digested.
0	0.2516 gram.	74.84 per cent.
Glycocholic, 0.03 per cent.	0.1993	80.07
Taurocholic, 0.10	0.3455	65.45
0.20	0.4332	56.68
0.50	0.4170	58.30

Here, the retarding influence of taurocholic acid is very manifest, while, on the other hand, the small percentage of glycocholic acid appears to increase the action of the ferment.

In view of the possible acid-reacting character of the contents of the small intestines, it becomes an interesting point to ascertain the influence of bile on the action of trypsin in the presence of more or less combined acid. With a pancreatic juice in which the proteids were partially saturated with salicylic acid, 0.1 per cent. combined acid being present, the following results were obtained:

Bile.	Weight of undigested fibrin.	Fibrin digested.
0 per cent.	0.4822 gram.	51.78 per cent.
1.0	0.4858	51.42
10.0	0.4091	59.09

This increased action in the presence of 10 per cent. of bile accords with Lindberger's results, this experimenter having found that bile in the presence of small percentages of (combined?) acetic and lactic acids tends to diminish the retarding effect produced by the acids alone.

In the presence of combined hydrochloric acid, the bile salts produced no effects whatever; the trypsin was entirely without action.

A METHOD OF DETERMINING THE VALUE OF ZINC DUST.

By H. N. Morse.

The apparatus and method here described were devised for the purpose of determining with a reasonable degree of accuracy the volume of hydrogen which metals will yield when they are treated with acids or alkalis. The present article is, however, limited to their application to the determination of the value of zinc dust.

It is believed that the results obtained by this method will be found to compare favorably with those reached by the excellent method of Fresenius,[1] that the skill demanded of the operator is not greater, and that the time required for a determination is considerably shorter.

The apparatus (Fig. 1) consists of the following parts:

[1] Zeit. ann. Chem. **17**, 465.

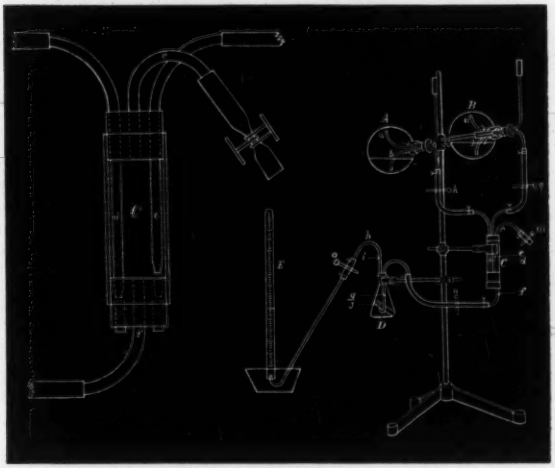


FIG. 1.

1st. Two flasks, *A* and *B*, each having a capacity of 750 or 1000 cc. One serves as a reservoir for distilled water, the other for dilute hydrochloric acid. Each flask is supplied with a rubber stopper, through which two small glass tubes *aa* and *bb* pass. The tubes *aa* connect the space above the liquids in the flasks with the outer air, and allow the gases expelled from the liquids by boiling to escape. The tubes *bb* dip under the surface of the liquids and serve to conduct them to other parts of the apparatus. The flasks *A* and *B* are filled to the level of the lower side of their necks by pulling the stoppers far enough forward to admit of the insertion of a funnel tube, the stem of which has been bent to a right angle. The contents of the flasks are boiled to expel the air absorbed in them.

2d. The arrangement *C*, which is a simple substitute for a three-way stopcock. The outer tube of *C* has an internal diameter of about 15 mm. and a length of about 70 mm.

It is supplied with two rubber stoppers, each of which has three perforations. The upper stopper carries the tube *c*, which

terminates at its lower surface; and the movable tubes *d* and *e*, which, when they are pressed down, enter corresponding holes in the lower stopper, and thus cut off the flow of liquids from A and *B* into *C*. The holes in the upper stopper through which *d* and *e* pass are lubricated with vaseline. The lower half of the holes into which *d* and *e* enter when they are pushed down is closed with glass plugs. The tubes *C* and *d* and *C* and *e* are connected by means of pieces of rubber tubing, each of which is supplied with a Mohr's pinch-cock. A short piece of rubber tubing with a pinch-cock is also slipped over the end of the tube *c* so that it may be opened or closed at will. The tube *f* terminates at the upper surface of the lower stopper, and serves to connect *C* with the flask in which the decomposition is effected.

To fill *C* from the flask *A* or *B*, the tube *d* or *e*, as the case may require, is raised, the pinch-cocks *m* and *k*, or *q*, are removed, and the liquid started down the tube *c* by sucking with the mouth at the end of the tube *c*. *C* then fills, the air being expelled through *c*. By closing *m* and opening *n* the liquid is made to pass on into the generating flask.

3d. An Erlenmeyer flask *D*, having a capacity of 50, 60 or 70 cc. The rubber stopper of this flask carries an inlet tube *g* and a delivery tube *h*, the forms and positions of which are sufficiently clear from the figure. A part of the vertical portion of the tube *h* should be filled with small fragments of broken glass, which may be kept in their proper position by allowing the end opening into the flask to soften and contract in the flame.

The zinc dust is placed in the small preparation tube *J*, and prevented from leaving the same by means of a filter of glass wool.

The tube and flask must be of such relative proportions that the open end of the former is somewhat elevated when the tube is in position in the flask. However, the space between the edge of the tube and the side of the flask must not be so great at any point as to allow the glass wool to escape from the tube. A little attention to this point is quite essential to the success of the method. The glass wool employed should be of the best quality, that is, the fibres should be long and elastic.

4th. A calibrated 100 cc. gas measuring tube *E*, which is filled with recently boiled, and still hot, water.

The rubber tubing employed in making the various connections should have thick walls and be of the best quality.

Tubing and stoppers which yield gas when treated with acids must, of course, be carefully avoided.[1] All rubber parts of the apparatus should be boiled in hydrochloric acid before they are used.

The determination is made in the following manner:

A weighed quantity of the zinc dust (0.200 to 0.240 gram) is placed in the bottom of the tube *J*. Enough water, which has been freed from air by boiling, to fill the tube about one-fourth full is introduced. The dust and water are then thoroughly mixed by means of a stout platinum wire or a small platinum spatula. The dust quickly subsides after the stirring has ceased, and any particles adhering to the platinum can be readily washed off by dipping it into the clear supernatant liquid.

A small bunch of glass wool, which has been freed from air by pressing it between the fingers under water, is now introduced and pressed down lightly upon the zinc dust. If it is believed that the quantity of glass wool already introduced is not sufficient to constitute a perfect filter, more is added; but an unnecessarily large quantity of the wool should be avoided, because of the obstruction which it offers to the passage of the gas out of the tube and the acid into it.

If gas bubbles lodge in or under the glass wool while it is being pressed down, they are dislodged, and brought to the surface by means of a platinum wire.

The tube having been placed in position, the whole apparatus is filled with water, and then with acid from *A* and *B*; both water and acid having been thoroughly boiled.

The acid is allowed to act for some time upon the zinc dust before heat is applied, in order that the finer material, which is most likely to be carried through the filter, may be slowly and quietly dissolved. Afterwards a small flame is placed under the flask. It generally happens that the hydrogen generated in the bottom of the tube crowds the wool up into the other end and against the side of the flask; but, if the tube and flask have been properly selected and the tube properly filled, there is no danger that either the wool or the dust will escape. The crowding of the wool into the open end of the tube, however, obstructs the entrance of the acid; but this difficulty can be remedied by occasionally applying the flame to the side of the flask directly in front of the mouth of

[1] Much of the American rubber now offered for sale yields large quantities of gas when treated with dilute acids.

the tube. Toward the end of the operation, when the hydrogen generated is mixed with a large proportion of steam and acid vapor, the tube can be readily filled with acid by opening the pinch-cock *n*, and allowing some of the cooler acid in *C* to flow into *D*.

The alloy of lead and zinc, which appears to be a constant constituent of zinc dust, decomposes quite slowly in dilute acids, and great care must be taken not to discontinue the operation until all evolution of hydrogen has ceased.

Hydrochloric acid is preferred for this decomposition, because it decomposes the lead-zinc alloy more rapidly than sulphuric; and because, being volatile, it dissolves the zinc dust which is lodged in the glass wool, even when the wool is not immersed in the liquid acid.

Before reading the volume of the gas collected, the tube *E* must, of course, be placed in a cylinder of water to which a little caustic soda has been added, in order to remove any carbon dioxide and vapor of hydrochloric acid which may be present.

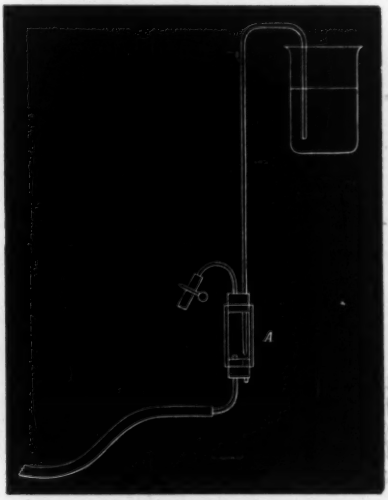


FIG. 2.

Fig. 2 represents a very simple substitute for the parts *A*, *B* and *C* of Fig. 1, which would probably be preferred by one who had only a small number of determinations to make. When this is used the water and acid are boiled in beakers, which are brought, one after the other, into the indicated position. The filling of *A*, Fig. 2, is accomplished in the same manner as that of *C*, Fig. 1.

The apparatus and method just described were placed in the hands of Messrs. W. H. Emerson and C. W. Hayes, students in this laboratory, to be tested with reference to the agreement of results which may reasonably be expected from them. Both used the same specimen of zinc dust. Mr. Emerson made four determinations, Mr. Hayes six. All of the results obtained by these gentlemen are recorded in the following statement:

Wt. of dust.	Vol. H_2 obtained.	Calc. wt. of Zn.	Per cent. Zn found.
0.2519 gram	77.14 cc.	0.22486 gram	88.87
0.2507	76.44	0.22282	88.80
0.20035	61.30	0.17869	89.13
0.2270	69.26	0.20188	88.93
0.2443	74.25	0.2164	88.60
0.2137	65.33	0.1904	89.10
0.2453	74.58	0.2174	88.62
0.2448	74.73	0.2178	88.97
0.2410	73.58	0.2145	88.95
0.2422	73.91	0.2154	88.94

An attempt was made to determine the value of zinc dust by amalgamating the metallic portions with mercury and weighing the amalgam. It was found that the metallic zinc contained in the dust is rapidly dissolved by the mercury in the presence of a one per cent. solution of tartaric acid, and that the quantity of hydrogen gas given off during the time required for the amalgamation is quite insignificant. Nevertheless the results were not satisfactory because of the difficulty with which the particles of dirt which collect upon the surface of the amalgam are removed.

Chemical Laboratory, Johns Hopkins University.

TWO FORMS OF APPARATUS WHICH FACILITATE THE CORRECT READING OF GAS-VOLUMES OVER WATER.

By H. N. Morse.

Every one who has had occasion to measure gases in the ordinary manner over water—that is, by raising the eudiometer above the water in the immersing cylinder until the liquid inside and outside of it stands on the same level—is familiar with a very disquieting experience. The volume of the gas quickly contracts in consequence of the cooling effect produced by the evaporation from the wet surface of the tube, which is now exposed to the air. As soon as the tube is raised into position the contraction begins; and if the condition of the atmosphere is such as to favor evaporation, it progresses very rapidly. However quickly the volume of the gas may have been noted, one rarely feels quite satisfied that the reading has not been affected by a change in temperature from this cause.

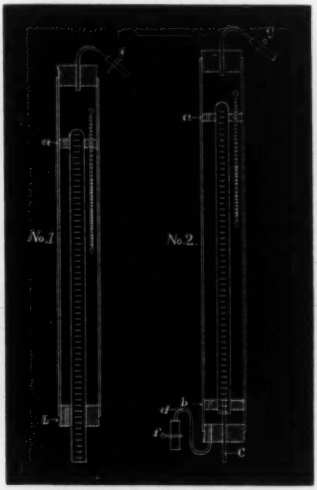


Fig. 1. Fig. 2.

Either of the simple arrangements represented in figures 1 and 2 will obviate the difficulty. The first (Fig. 1) is to be used in connection with an immersing cylinder. The second (Fig. 2), without it. In both cases the eudiometer is fastened quite firmly into a clear glass tube by means of the corks *a* and *b*, all of which are perforated in order to allow the water to pass freely up and down. The corks *aa* carry thermometers. The eudiometer in No. 1 projects below, while that in No. 2 is wholly included in the jacket tube. Each apparatus is closed at the top by a stopper, through which a small glass tube passes. The lower end of No. 2 is closed by a cork, which carries two tubes *c* and *d*. The tube *c* receives the gas from the delivery tube, and conducts it into the eudiometer; while *d* serves as an overflow tube for air or water. The cork used in constructing these pieces of apparatus should be thoroughly soaked in molten paraffine.

The method of using No. 1 is as follows: it is inverted, and the eudiometer filled in the usual manner. When it is transferred to the immersing cylinder, the pinch-cock *e* is removed and the jacket allowed to fill with water. When it is desired to read the volume of the gas, the pinch-cock is replaced and the apparatus drawn up until the water inside of the eudiometer and outside of the jacket stands on the same level. The jacket remains filled with water having the same temperature as that in the cylinder, and protects the gas from any sudden changes in temperature. No. 2 is inverted, the pinch-cock *f* removed, and the whole apparatus filled with water until the tube *d* overflows; when *f* is replaced, and the remainder of the tube *c* which lies above the level of the outlet of *d* is filled.

The apparatus is now placed over the delivery tube in the usual manner. The gas having been collected, *c* is closed by means of a tightly fitting stopper, and the apparatus removed to a clamp stand and fastened in a vertical position and at a convenient height. When the volume of the gas is to be ascertained, the pinch-cock *g* is removed, and the water in the jacket allowed to descend through *d* to the proper level by opening *f*. The space in the jacket thus vacated by the water being saturated with aqueous vapor, retains for a considerable time the temperature of the water. If it is desired to treat the gas with absorbents, they can be introduced by removing the upper stopper and pouring them into

the jacket, the level of the liquid previously contained in it having been lowered to any extent which may seem expedient. The succession of meniscuses which is obtained when the liquid in the jacket is lowered to the level of that in the eudiometer, considerably facilitates the correct reading of the volume of the gas.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

AN APPARATUS FOR THE PURIFICATION OF MERCURY BY DISTILLATION IN A VACUUM.

BY H. N. MORSE.

The essential parts of the apparatus are an ordinary combustion tube, *a*, about 450 mm. long, which has been drawn out at the ends, *b* and *c*, in the manner indicated in the figure; and two pieces of barometer tubing, *d* and *e*.

b and *d* are connected by means of rubber tubing; *c* and *e* by means of a tightly fitting rubber stopper. A mercury cup is placed over each of these joints to prevent leakage.

The tube *e* projects into the large end of *c* to some distance above the stopper, in order that the lower portion of *c* may fill with mercury, and thus protect the stopper from the hot metal which falls from above.

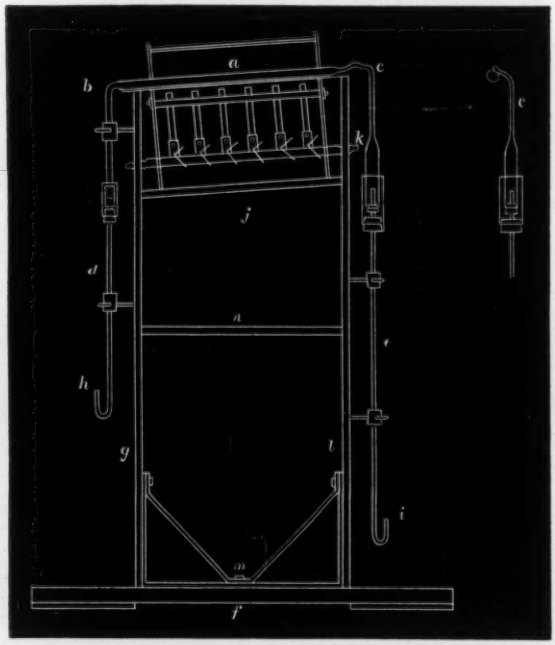
The distance between *b* and *h* is about 770 mm. The length of the tube *e* above *i* should not be less than 825 mm.

The turned-up ends of *d* and *e* should have a length of 60 mm., or a length more than sufficient to compensate the greatest variations of atmospheric pressure.

b and *c* make such angles with *a* that they remain vertical when the front end of *a* is raised about 15 mm. (a distance equal to the internal diameter of the tube) above the back end. The apparatus is held in position by means of a wooden stand which consists of a base and two uprights, *f*, *g* and *l*; a double bracket, *m*; a brace, *n*; and a movable shelf, *j*.

The tube *a* is placed in a sheet-iron trough which rests in a groove in the upper ends of the uprights *g* and *l*. The tubes *d*

and *e* are fastened to the uprights by means of hooks and rubber stoppers or corks. The hooks should be somewhat open, so that, after slipping the stoppers out of them, the apparatus as a whole may be removed from the stand. Good hooks for this purpose are obtained by filing off the turned-in end of ordinary screw eyes.



The tube *c* is turned to one side, if necessary, in order to avoid the rubber tubing through which the gas is brought into the furnace at *k*.

To set the apparatus in operation, the lower end of the tube *d* is immersed in a narrow cylinder containing some of the mercury

to be distilled. A Sprengel pump is then attached to *i* and the apparatus exhausted. By raising or lowering the cylinder in which *h* is immersed, the mercury is brought to the proper level in *a*; after which the lamps beneath are lighted. The flames should be made as small as possible at the beginning of the distillation, and the temperature should never be allowed to rise so high as to produce any visible commotion in the distilling mercury.

The tube *c* being cool during the first part of the distillation, the rubber stopper connecting *c* and *e* is not injured by the mercury which falls upon it. After the lower end of *c* has been once filled and the mercury has begun to descend through *e*, there is no danger of overheating the stopper, however rapidly the distillation may proceed.

When enough mercury has been distilled to fill *e* to the barometric height, the Sprengel pump is detached. The working of the apparatus is afterwards automatic. Whenever it is desired to distill a quantity of mercury, it is also necessary to place a cylinder containing it over *h* and light the gas under *a*.

The action of *e* and its connections being that of a Sprengel pump, the vacuum is never more than temporarily impaired.

The apparatus can also be brought into working order without the use of a Sprengel pump by attaching a long glass tube in a vertical position to *h*, and filling *a* through it to the proper level, and then distilling until a vacuum is produced.

The distillation of mercury by this arrangement is quite rapid; and when it is once in operation it requires no attention, except that of keeping the mercury in the feeding cylinder at something near the proper level. An automatic arrangement for this purpose is quite desirable.

SOME EXPERIMENTS ON THE RELATION OF ANTISEPTIC POWER TO CHEMICAL CONSTITUTION.

By J. R. Duggan.

The following paper is, as the title states, simply an account of some experiments, with no attempt at anything farther; and they are offered more as a suggestion towards future work than for any value of their own. I hope that in the future they may be extended

to such a number of compounds, and with such accuracy, as to be of some use in the study of the physiological action of organic bodies whose chemical structure has been previously determined. Of course the step from the minute organisms to the vertebrate body is an immense one, but in each case we must study the action on single cells, and where these are separate and undifferentiated the conditions are much easier to control and the problem much simpler. One can scarcely hope for a perfect science by which the physiological action of a compound can always be foretold from its chemical constitution, but there is certainly reason to expect that we may in time be able to trace certain general laws that apply to classes of compounds and groups of atoms; and with this ultimate view the following experiments have been undertaken.

The method used to determine antiseptic power consisted in adding to 10 cc. of a standard solution of beef peptones the requisite quantity of a solution of the compound and water enough to make the whole measure 20 cc. This was placed in a small flask stoppered with cotton, and heated just to boiling in order to kill any organisms present. In the case of alcohols and other easily volatile bodies, the flask was tightly corked before heating to avoid loss by evaporation. After cooling, the cotton plug was lifted with a pair of sterilised forceps, and a few drops of a culture fluid containing only *Bacillus subtilis* added to the solution. This precaution was found necessary, not so much to prevent the presence of other bacteria, as to keep out spores of penicillium and mucor. These develop readily under conditions that prevent entirely the growth of bacteria, and thus interfere with results.

A series of flasks thus prepared were placed in a warm chamber kept at about 36° C., and examined twice daily. The cloudiness of the solution was found to be the best indication of the development of the bacteria, although microscopic examinations were frequently made. The point in view has been to find what quantities of the various substances under consideration would give an equal restraining influence, and not to determine the amount that entirely prevents development. The approximate standard was a flask giving slight cloudiness in 48 hours and considerable in 72.

The method in itself seems very simple, but in practical working several difficulties introduce themselves, and interfere considerably with the accuracy and reliability of results. For example, some of the flasks, especially those containing phenol and the acids of

the marsh gas series, frequently show a slight cloudiness which does not increase, or at least very slowly, on standing. It has occurred to me that this might be due to the products of putrefaction formed, and which thus increase the amount of these agents to an extent that prevents further development.

The following table is a list of the substances whose restraining influence has been determined with approximate accuracy, and of the amounts required in parts per 10,000 of the solution:

Oxybenzoic acids, $C_6H_4(COOH)(OH)$.		
Salicylic acid	(1 : 2) . .	4
Oxybenzoic acid	(1 : 3) . .	6
Paraoxybenzoic acid	(1 : 4) . .	8
Phenols, $C_6H_5(OH)_x$.		
Phenol, $C_6H_5(OH)$	. . .	20
Pyrocatechin, $C_6H_4(OH)_2$	(1 : 2) .	20
Resorcin, $C_6H_4(OH)_2$	(1 : 3) . .	25
Hydroquinone, $C_6H_4(OH)_2$	(1 : 4) .	30
Pyrogallol, $C_6H_3(OH)_3$	. . . .	15
Alcohols, $RCH_3(OH)$.		
Methyl alcohol, $CH_3(OH)$	. .	300
Ethyl alcohol, $C_2H_5(OH)$	. .	500
Propyl alcohol, $C_3H_7(OH)$	normal .	200

In addition to the above the three acids, formic, acetic, and propionic, have been experimented upon to determine both their antiseptic and their germicide power. Accurate conclusions have not yet been reached on their restraining influence, but it is evidently considerable, and is not in the order of their corresponding alcohols, propionic being lowest in the series, and formic the highest. Their germicide power was tested by exposing spores of *B. subtilis* to their action for two hours. The amounts required to destroy these were of formic, 7 per cent.; of acetic, 9 per cent.; and of propionic, 12 per cent. It will be seen that these figures are pretty nearly in an inverse ratio to the acidity of these acids, that is, the amount of any base which they can saturate.

The first two classes in the above table seem to show that ortho compounds are the most antiseptic, and the para the least so,

but it will be necessary to examine a larger number of substances before this conclusion can be stated as a general one.

It will be noticed that the alcohols show a peculiar order, for which I can suggest no explanation. A few other surmises, such as the influence of the hydroxyl group, might be offered, but I prefer to leave these for another paper, in which it is intended to include experiments in a much larger number of compounds on which to base conclusions.

JOHNS HOPKINS UNIVERSITY.

ON SOME PROPERTIES OF PHENYLSULPHONACETIC ETHERS.[1]

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

II.

In the first communication on this subject it was shown that in ethyl phenylsulphonacetate the combined negative influence of phenylsulphuryl and ethylcarboxyl on methylene sufficed to render one of the hydrogens of the latter group replaceable by sodium; and, by the action of benzylchloride on the sodium derivative, benzyl could be introduced in place of sodium. In the present note we shall show that a method of obtaining substitution derivatives of cinnamic acid may be based on the properties of above compounds, and that alkyl iodides act on the sodium derivatives in the same manner as benzylchloride, forming alkylphenylsulphonacetates. The examination of this class of compounds has called renewed attention to their similarity with acetylalkylacetates, inasmuch as when they are heated with alkalis they decompose into phenylalkylsulphones and alkaline carbonates: a reaction corresponding to the decomposition of acetylalkylacetic ethers into alkylacetones and carbonates.

Action of alcoholic caustic potash on phenylsulphonacetic ether.

Two grams of the ether and four grams of caustic potash were dissolved in about ten grams of alcohol and the solution heated

[1] This Journal 5, 116.

to 140° for five hours. The contents of the tube was evaporated on a water-bath, and water added to the residue. An insoluble oil remained, which soon solidified, and was purified by crystallisation from hot water. The analysis gave the following results:

0.3878 gram of substance gave 0.7612 gram of CO_2 and 0.1858 gram of H_2O.

	Theory for $C_6H_5SO_2CH_3$.	Found.
C	53.8	53.5
H	5.1	5.3

The substance crystallises from hot water as tabular plates, and melts at 88°. It is identical with the phenylmethylsulphone obtained synthetically from sodium phenylsulphinate and methyl iodide,[1] and its formation may be represented as follows:

$$C_6H_5SO_2CH_2COOC_2H_5 + 2KOH = C_6H_5SO_2CH_3 + K_2CO_3 + C_2H_6O.$$

This sulphone has been obtained by four different methods:[1] by the action of sodium phenylsulphinate on methylene-iodo-phenylsulphone; by the action of alkylsodiumoxides on the same compound; by the action of methyliodide on sodium phenylsulphinate; and by the action of alkalis on phenylsulphonacetic ether. It is evident that the introduction of phenylsulphuryl in the methyl of acetic acid shows itself in loosening the affinity between the two linked carbon atoms; an effect which is also produced by other negative groups, as acetyl and ethylcarboxyl.

Action of ethyl iodide on sodium phenylsulphonacetic ether.

To a solution of one gram of sodium in absolute alcohol, an alcoholic solution of 10 grams of phenylsulphonacetic ether (1 mol.) was added, and, finally, 6.8 grams of ethyl iodide. The mixture was heated in a flask connected with reflux-cooler until it had lost its alkaline reaction; it requiring from five to six hours for the quantities taken. The alcohol was then distilled off, the residue poured into cold water, and allowed to stand until it became solid. The substance was purified by repeated crystallisation from dilute alcohol. The sulphur estimation gave the following result:

0.3332 gram of substance gave 0.3096 gram of $BaSO_4$.

	Theory for $CH{<}^{C_6H_5}_{SO_2C_6H_5}_{COOC_2H_5}$	Found.
S	12.5	12.7

[1] This Journal **6**, 253.

Ethylphenylsulphonacetic ether crystallises from dilute alcohol as rhombic prisms, melting at 62°. It is readily soluble in ether, benzene, ethylacetate, moderately in ligroin, insoluble in water. The addition of sodium ethyl oxide to the alcoholic solution forms a precipitate of the sodium derivative which is more soluble than that of phenylsulphonacetic ether. This compound heated with alcoholic potash undergoes a decomposition similar to that of phenylsulphonacetic ether. Five grams of the ether and seven grams of caustic potash were dissolved in alcohol and heated in a sealed tube for five hours at 140°. The product was treated as already described for methylphenylsulphone, with the difference that the residue was purified by crystallisation from ligroin to which a few drops of acetic acid were added.

0.3247 gram of substance gave 0.6922 gram of CO_2 and 0.1877 gram of H_2O.

0.3693 gram of substance gave 0.7940 gram of CO_2 and 0.2237 gram of H_2O.

	Theory for $C_6H_5SO_2C_2H_7$.	Found.	
C	58.7	58.1	58.7
H	6.5	6.4	6.7

Propylphenylsulphone crystallises from ligroin as large rhombic plates, melting at 45°, and has an odor resembling that of crotonic acid. It is insoluble in water, but readily soluble in ether, chloroform, alcohol and acetic acid.

The formation of the sulphone may be represented as follows:

$$\left.\begin{matrix}C_6H_5SO_2\\C_2H_5\end{matrix}\right\rangle CH-COOC_2H_5+2KOH$$
$$=C_6H_5-SO_2-C_3H_7+K_2CO_3+C_2H_5OH.$$

It does not appear possible to introduce ethyl into the monoethyl derivative, at least not by the method previously used. A solution containing sodium ethyl oxide, ethyl sulphone-ether and ethyl iodide, heated until it showed no alkalinity, gave nothing but unchanged ethylphenylsulphonacetic ether.

Action of allyl iodide on sodium phenylsulphonacetic ether.

The allyl derivative was prepared by heating an absolute alcoholic solution of ethyl sodium phenylsulphonacetate with allyl iodide until the solution became neutral. The new substance was precipitated from the alcoholic solution on addition of a sufficient quantity

of water, as an oil; and, after standing several hours, solidified to a crystalline mass. It was purified by several crystallisations from dilute alcohol, and was ethyl allylphenylsulphonacetate, as shown by the following sulphur estimation:

0.2882 gram of substance gave 0.2558 gram of $BaSO_4$.

	Theory for $C_6H_5SO_2>CH\text{-}COOC_2H_5$.	Found.
S	11.9	12.19

The compound crystallises from alcohol as rhombic prisms, melting at 64.5°. They are soluble in alcohol, ether and acetic acid, insoluble in boiling water.

The decomposition of ethylphenylsulphonacetate by alkalis into methylphenylsulphone and carbonate led us to expect the formation of allylphenylsulphone in the decomposition of the allyl derivative. An alcoholic solution of the compound and caustic potash was heated four hours at 120°, and, after inspissation, water and sufficient acid to neutralise the alkaline solution were added. The liquid was extracted several times with ether, and the ethereal solution deposited, on evaporation of the ether, long white crystals. These crystals may be crystallised from ligroin to which a few drops of alcohol are added; or better from acetic acid. The substance forms long prismatic needles, resembling those of phthalic anhydride. We were unable to obtain this substance in a state suitable for analysis, as it gradually changes into an amorphous compound; a change which takes place more rapidly the purer the substance.

Although a number of crystalline allyl compounds show a similar change to an amorphous state, it did not seem probable that allylphenylsulphone should show this property in so marked a degree; and we found by preparing that substance from allyl iodide and sodium phenylsulphinate that it is a heavy oil, which does not change on long standing. The sulphone adds bromine to form a crystalline substance. We intend to make these reactions the subject of further investigation.

Action of benzylchloride on ethyl sodium phenylsulphonebenzylacetate.

The endeavor to replace more than one hydrogen of phenylsulphonacetate by ethyl was not successful; but, on the other hand, the introduction of two benzyl takes place readily, yielding quantitative results.

The dibenzyl derivative was prepared by heating equivalent quantities of the sodium derivative of the monobenzyl compound with alcohol and benzylchloride to 100° for several hours. On evaporating the alcohol, the addition of water caused an oily substance to separate, which soon solidified, and was purified by crystallising from alcohol.

A sulphur analysis gave the following numbers:

0.2464 gram of substance gave 0.1390 gram of $BaSO_4$.

	Theory for $\frac{(C_6H_5CH_2)_2}{C_6H_5SO_2}\!>\!C\!-\!COOC_2H_5$.	Found.
S	7.8	7.75

Ethyl dibenzylphenylsulphonacetate crystallises from alcohol in white plates, melting at 118°. It is soluble in hot alcohol, moderately in cold; the insolubility of benzyl derivatives of phenylsulphonacetate increasing with the number of benzyl in the compound. The substance does not form a sodium derivative.

In a former paper[1] it was shown that benzylphenylsulphonacetate is decomposed by caustic alkalis into salts of phenylsulphinic and cinnamic acids; whereas the alkyl derivatives are decomposed by the same treatment into sulphones and carbonates. The dibenzyl compound undergoes the decomposition characteristic of the monobenzyl derivative, it yielding a benzylcinnamic acid.

Tubes containing three grams of the dibenzyl compound, five grams of caustic potash, and enough alcohol to dissolve them, were heated to 160° for six hours, and after the alcohol was driven off, acidified with sulphuric acid, and the product of the reaction extracted with ether. On evaporation of the ether a crystalline substance remained, which was purified by several crystallisations from acetic acid. The acid was analysed with the following results:

0.2935 gram of substance gave 0.8697 gram of CO_2 and 0.1767 gram of H_2O.

0.2346 gram of substance gave 0.6980 gram of CO_2 and 0.1432 gram of H_2O.

	Theory for $\frac{C_6H_5CH}{C_6H_5CH_2}\!>\!C\!-\!COOH$.	Found.	
C	80.6	80.8	81.1
H	5.8	6.6	6.7

[1] This Journal **5**, 119.

Benzylcinnamic acid is found according to the following equation:

$$\begin{matrix} C_6H_5SO_2 \\ C_6H_5CH_2 \end{matrix}\!\!>\!CH-COOC_2H_5 + 2KOH =$$

$$\begin{matrix} C_6H_5CH_2 \\ C_6H_5CH \end{matrix}\!\!>\!C-COOK + C_6H_5SO_2K + C_2H_5OH + H_2O.$$

The acid forms large white needles, looking like those of phthalic anhydride, and melting at 157°. It is insoluble in water and ligroin, easily soluble in alcohol, chloroform, ether, benzene and acetic acid when warm, moderately soluble in these liquids in the cold.

It dissolves readily in alkalis, forming soluble salts. The sodium salt was obtained by heating the acid with an amount of caustic soda insufficient to dissolve it, filtering and evaporating. It is a crystalline substance, and is very soluble in water. A sodium estimation gave as below:

0.1852 gram of salt, dried at 140°, gave 0.534 gram of Na_2SO_4.

	Theory for $\begin{matrix} C_6H_5CH \\ C_6H_5CH_2 \end{matrix}\!\!>\!C-COONa$.	Found.
Na	8.8	9.3

The silver salt is obtained by adding silver nitrate to the solution of the sodium salt, and consists of pearly rhombic plates that are but slightly soluble in cold water. Treated with nascent hydrogen benzylcinnamic acid takes up hydrogen, passing over into hydrobenzylcinnamic acid. An alkaline solution of the unsaturated acid was treated with sodiumamalgam until no further action was noticed, and the precipitate obtained by addition of an acid crystallised several times from dilute acetic acid. This compound was analysed with the following result:

0.3314 gram of substance gave 0.9758 gram of CO_2, and 0.2075 gram of H_2O.

	Theory for $(C_6H_5CH_2)_2CH-COOH$.	Found.
C	80.0	80.3
H	6.6	6.9

Dibenzylacetic, or hydrobenzylcinnamic, acid crystallises as tabular prisms, melting at 87°. It is slightly soluble in hot water, very soluble in alcohol, acetic acid, benzene and chloroform. It dissolves its alkalis, forming salts. The addition of silver nitrate to a solution of the sodium salt gave the silver salt as rhombic prisms that are soluble in boiling water.

0.2238 gram of silver salt gave 0.0902 gram of AgCl.

	Theory for $(C_6H_4CH_2)_2COOAg$.	Found.
Ag	31.2	30.3

We had hoped to make use of the derivatives of phenylsulphonacetic ether, to contribute to the question of the equal value of the four carbon affinities. Our experiments consisted in endeavoring to introduce benzyl into the ethylsulphone compound, and ethyl into the benzyl derivative; the object in view was to ascertain whether both these reactions would yield the same compound. The products of the action of ethyl iodide on benzylphenylsulphonacetate and benzylchloride on ethylphenylsulphonacetate solidified only on long standing. We were unable to obtain from these products any other compounds in a pure state than the substances used as starting points.

TUFTS COLLEGE, MASS., *April* 3, 1885.

NOTE ON THE CONSTITUTION OF THE ADDITION-PRODUCT OF CHLORHYDRIC ACID TO ETHYLCYANIDE.

BY ARTHUR MICHAEL AND JOHN F. WING.

The nitriles of organic acids possess in a marked degree the property of uniting with halogens and halhydric acids, to form a series of interesting compounds, the constitution of which is still more a matter of conjecture than certainty. These compounds are sometimes classed as belonging to the so-called molecular compounds; again, as unstable chemical compounds. It is becoming more and more evident that a much greater degree of precaution is necessary in judging of the constitution of compounds belonging apparently to the same class, but either of a different series, or one whose radical has undergone a slight modification, than is at present customary. The replacement of a positive element like hydrogen by an atom of a negative element or negative group cannot fail to cause a readjustment of the affinities of the constituent atoms, and the atomic arrangement and stability of a

molecule may be dependent on such an interchange. Unless a thorough investigation of the two products is made, no great confidence can be given to a classification which places them in the same group.

The investigation of the compounds of halhydric acids with nitriles is of interest, as these compounds show properties which would seem to place them in the class of so-called double compounds. Again, they show properties which indicate a chemical union between the constituent substances. The compounds may be grouped into three classes, which are, considered as double compounds, R—CNHCL, 2R—CN,3HBr, and R—CN,2HBr; as chemical compounds, the constitution R—CClNH and R—CCl_2—NH_2 are adopted for the first and last, and we suggest $R-CBr<\begin{matrix}N-CBr-R\\NH_3Br\end{matrix}$ for that of the middle class of compounds. The main reason for believing that they are chemical compounds is that they unite readily with water, forming ammonium salts and organic acids, under conditions of temperature that aqueous halhydric acids do not react on nitriles. But it must be remembered that, even if they are considered as double compounds, these are very different from a mixture of a nitrile and halhydric acid; besides that the former is soluble in water and, therefore, much more susceptible to its action, whereas the latter substances do not mix. It is evident that more cogent reasons must be sought for before the constitution of these compounds can be considered as definitely established; and, in the hope of contributing to this question, we have taken up the investigation of their behavior towards certain reagents.

The subject of the present note is the addition-product of chlorhydric acid to ethylcyanide, a substance that we prepared according to the directions of the discoverer.[1] The compound is probably the most stable of the compounds formed by the union of halhydric acids with nitriles; it may be crystallised from cold water without change, and also dissolves in alcohol without decomposition.

We have examined the action of sodium phenyl oxide and aniline on the compound, and have obtained results which are of value in judging the constitution of the substance. The nitrile compound, dried *in vacuo*, was dissolved in cold absolute alcohol, and somewhat less than the equivalent amount of aniline, also

[1] Gautier, Ann. de Chim. et Phys. [4] **17**, 184.

dissolved in alcohol, added. A reaction took place almost immediately and was shown by the solution becoming warm. In our experiments the solution was kept cold. The solution was allowed to stand several hours in a closed vessel, and then the alcohol evaporated by exposure to the air at ordinary room-temperature. The residue was dissolved in water, caustic soda added, and the alkaline liquid shaken out with ether. On evaporation of the ether an oil remained, which gradually, in two or three days, solidified. The substance was pressed between bibulous paper, and dried *in vacuo*. A nitrogen estimation gave the following result:

0.1587 gram of substance gave 27.8 cc. of nitrogen at 745 mm. and 26°.

	Theory for $C_9H_{12}N_2$.	Found.
N	18.92	19.04

The substance crystallises in rhombohedrons, melting at 68°. It is insoluble in water, soluble in alcohol and ether. Boiled with water it decomposes into ammonia and propio-anilide, melting at 116°.[1] Boiled with chlorhydric acid it is decomposed into aniline chlorhydrate and propionic acid.

The substance has basic properties. It dissolves readily in cold acids, and is precipitated as an oil by addition of alkalis. Platinum chloride added to a solution of the chlorhydrate gives gradually a yellow precipitate of the double platinum salt. This salt consists of radial groups of prisms with oblique end-faces. When allowed to stand for a long time with chlorhydric acid, or immediately when heated with the acid, it is decomposed with the formation of platinum ammonium chloride.

The analyses of the salt, dried at 100°, gave the following figures:

0.3391 gram of platinum salt gave 23 cc. of N at 750 mm. and 20°.

0.2568 gram of platinum salt gave 0.2897 gram of CO_2 and 0.0847 gram of H_2O.

	Theory for $(C_9H_{12}N_2HCl)_2PtCl_4$.	Found.
C	30.59	30.76
H	3.59	3.66
N	7.93	7.65

The base $C_9H_{12}N_2$ is formed from propionitrile by the addition of aniline, and agrees in its properties with those of an amidine. The

[1] The melting point of this compound is given at 92° (Sestini, Zeitsch. chem. 1871, 35). The melting point of a product prepared from pure propionic acid and aniline was as stated above.

substance may be called propenylphenylamidine, and the formation of its chlorhydrate is represented by the following equation:

$$C_2H_5CClNH + NH_2C_6H_5 = C_2H_5 - C\begin{matrix}NHC_6H_5HCl\\ NH\end{matrix}$$

The action of sodium phenyl oxide on the addition-product gave less satisfactory results, although they are not altogether without interest. An alcoholic solution of the two compounds reacted in the cold, depositing sodium chloride, and the filtrate gave, on evaporation of the alcohol, a heavy oil, which did not solidify on standing, or at a low temperature. It is a base, as it dissolves in acids, and is precipitated from the solution by alkalis. The base is somewhat soluble in water, and the solution shows an alkaline reaction. We were unable to obtain it in a state suitable for analysis, and equally unsuccessful were the attempts to obtain its salts. A solution of the base in ether treated with dry chlorhydric acid gave an amorphous precipitate, which was doubtless the chlorhydrate, but the compound decomposed on standing into phenol and other products. The addition of platinum chloride to a chlorhydric acid solution of the base gave a precipitate of ammonium platinum chloride. The base is probably formed according to the following reaction:

$$C_2H_5CClNH + NaOC_6H_5 = C_2H_5 - C\begin{matrix}OC_6H_5\\ NH\end{matrix} + NaCl.$$

We believe that the above results prove the constitution of the addition-product of ethylcyanide and chlorhydric acid to a reasonable certainty. If the substance is considered as the molecular compound—$C_2H_5 - CN, HCl$—the first action of aniline would be to unite with the chlorhydric acid, setting free the nitrile; the products of the reaction would be therefore aniline chlorhydrate and ethyl cyanide, and aniline chlorhydrate only acts on nitriles at a high temperature. The same reasoning applies to the action of sodium phenyl oxide; in that case free phenol and ethyl cyanide should be formed. The formation of a basic product shows quite conclusively that in the compound in question chlorhydric acid must be in chemical combination with the nitrile. The constitution of the compound is therefore $C_2H_5 - CCl - NH$, and it may be called propenylchloro-imine or chlorpropylidene-imine. We intend to make this substance the subject of further experimentation, and also to examine the two other classes of addition-products of halhydric acids and nitriles in a similar manner.

TUFTS COLLEGE, MASS., *April* 8, 1885.